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Defect-defect interactions in the silver halides with special application to pure silver chloride

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DEFECT-DEFECT INTERACTIONS IN THE SILVER
HALIDES WITH SPECIAL APPLICATION TO PURE
SILVER CHLORIDE.**

**Iowa State University of Science and Technology, Ph.D., 1967
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DEFECT-DEFECT INTERACTIONS IN THE SILVER HALIDES
WITH SPECIAL APPLICATION TO PURE SILVER CHLORIDE

by

Richard Anthony Sevenich

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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I. INTRODUCTION

The silver halides are face centered cubic crystals (see Fig. 1). The positively charged silver ions lie on their own face centered cubic sublattice as do the negatively charged halogen ions. A perfect crystal consists of these two intermeshed sublattices with each site occupied. At any finite temperature the ions have thermal energy and thus they vibrate about their equilibrium positions. Some of these vibrating ions have enough thermal energy to leave their perfect lattice sites and occupy other positions in the crystal. When this happens the pure crystal is said to be intrinsically disordered. Intrinsic Frenkel disorder (Frenkel 1926) occurs when an ion acquires enough thermal energy to move from its site on the perfect lattice to an interstitial position leaving behind a vacancy. The Frenkel defect pair consists of the interstitial ion and the corresponding vacancy.

Schottky disorder (Wagner and Schottky 1931) occurs when vacancies are introduced into the perfect lattice without corresponding interstitial defects. This can happen if an ion near the surface acquires enough thermal energy to jump to the surface leaving behind a vacancy. Adjacent ions on the same lattice may then jump into the vacant site so that the original vacancy is effectively able to migrate. The vacancy concentration on the cation sublattice must be

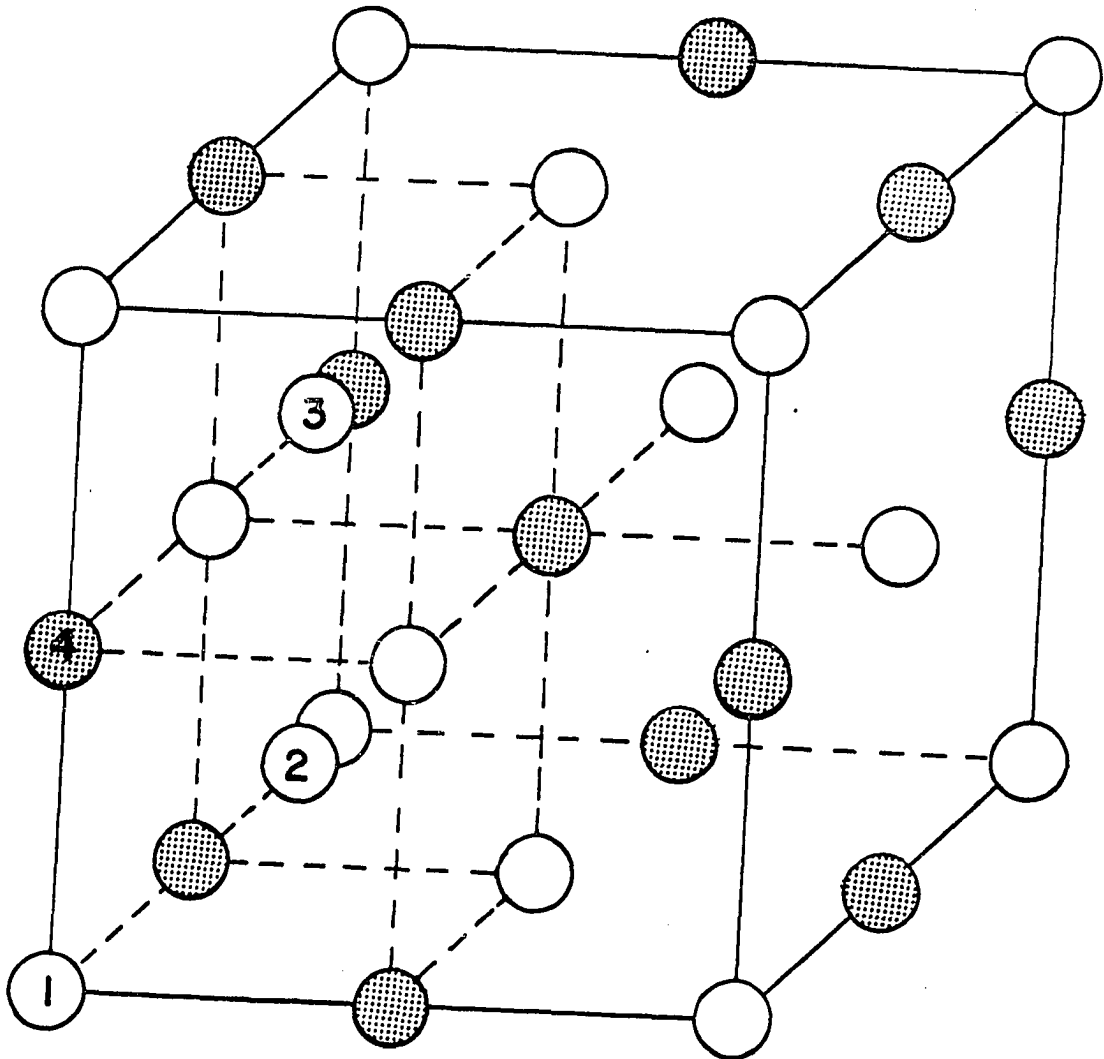


Fig. 1. Silver halide crystal structure

The anion sites are shaded. The four sites comprising the unit cell are labeled 1, 2, 3, and 4. Site 1 is a cation site. Sites 2 and 3 are interstitial sites.

equal to that on the anion sublattice so that electrical neutrality is preserved in the interior of the crystal. Other types of intrinsic disorder such as the occupation of a negative ion site by a positive ion (van Santen 1950) would occur too rarely to be of interest because of the high energy of formation required.

In the silver halides Frenkel disorder is the dominant disorder (Ebert and Teltow 1955; Compton and Maurer 1956; Koch and Wagner 1937; Kurnick 1952; Teltow 1949; Christy and Lawson 1951). The work of Fouchaux and Simmons (1964) has shown that the upper limit for the concentration of Schottky defects in silver chloride is 90 ppm at melting. This is to be compared to a concentration of Frenkel defects of about 350 ppm (Ebert and Teltow 1955).

The occurrence of intrinsic disorder can be explained using thermodynamic arguments. Consider the particular case of cationic Frenkel disorder since it is the appropriate disorder for the silver halides. Let N be the number of defect pairs present in a pure crystal at temperature T , B_V be the number of cation sites, and B_I be the number of interstitial sites. The Gibbs free energy of the crystal, assuming no interactions among defects, is given by

$$G(N, T, p) = G_0(T) + N h_F - N T \Delta S_{th} - T S_{cf}, \quad (1.1)$$

where G_0 is the Gibbs free energy of the perfect crystal, h_F is the enthalpy of formation of a Frenkel defect pair, S_{cf} is the configurational entropy, and ΔS_{th} is the change

in the thermal entropy upon the addition of a Frenkel defect pair. The condition for equilibrium is that

$$\left. \frac{\partial G(N, T, p)}{\partial N} \right|_{T, p} = 0. \quad (1.2)$$

The configurational entropy is given by

$$S_{cf} = k \log \left[\frac{B_V!}{N!(B_V - N)!} \frac{B_I!}{N!(B_I - N)!} \right], \quad (1.3)$$

where k is the Boltzmann constant. For $N \ll B_V \sim B_I$ we may employ the Stirling approximation to obtain from equations (1.1), (1.2), and (1.3),

$$\frac{N}{(B_V B_I)^{\frac{1}{2}}} = \exp [-(h_f - T\Delta S_{th})/2kT]. \quad (1.4)$$

If we define the Gibbs free energy of formation by

$$g_f = h_f - T\Delta S_{th}, \quad (1.5)$$

we can rewrite equation (1.4) as

$$\frac{N}{(B_V B_I)^{\frac{1}{2}}} = \exp [-g_f/2 kT]. \quad (1.6)$$

The dominance of cationic Frenkel disorder in the silver halides can be explained qualitatively on energetic grounds. We expect Frenkel disorder on the cation sublattice to occur more readily than that on the anion sublattice because the silver ion is significantly smaller than the halogen ion. Consider silver chloride. The radius of the chloride ion is 1.8 Å and the cation-anion separation is 2.8 Å. Hence the silver ion with its 1.0 Å radius can more easily fit into an interstitial site than can the larger chloride ion.

To discuss the competition between cationic Frenkel disorder and Schottky disorder it is illuminating to contrast the silver halides with the alkali halides. Schottky disorder is the dominant disorder in the alkali halides. The silver ion in a silver halide with its filled 4d shell has a higher polarizability than, say, the sodium ion in sodium chloride (Mott and Gurney 1964, p.7). Consider a pair of interacting ions. That part of the interaction energy associated with the fact the ions are polarized, the van der Waals energy, is of the form

$$- \frac{\alpha_1 \alpha_2}{r^6}, \quad (1.7)$$

where α_1 and α_2 are the polarizabilities and r is the separation of the ions (London 1930). Thus a silver ion with its significantly larger van der Waals attraction (Mayer 1933a; Mayer 1933b; Kurosawa 1957) finds it much easier to occupy an interstitial site than does the corresponding alkali ion, the increased van der Waals attraction of the nearby ions tending to compensate for the increased Madelung energy. The van der Waals attraction is evidently large enough to make the energy of formation of cationic Frenkel defects in the silver halides smaller than the energy of formation of Schottky defects.

So far we have spoken of the existence of intrinsic disorder. Impurities may occur in silver halide crystals as well. Some possible impurities are aliovalent anion or cation

impurities such as those formed by doping silver chloride with CdCl_2 . At low concentrations the Cd^{++} ion will be incorporated into the crystal at a cation lattice site (Mott and Gurney 1964, p.46). To preserve electrical neutrality there must appear a corresponding cation vacancy.

The study of disorder in the silver halides, as in the other ionic crystals, is of fundamental importance. For example, because the silver halides have tightly bound electrons in closed shells, both conduction and diffusion are ionic in character. That is, charge cannot be carried through the perfect crystal; there must be defects present. The comprehensive review article by Lidiard (1957) treats the above questions in detail. The physical properties mentioned above clearly depend on the number of defects present, so a correct theoretical value for the concentration of defects is vital. In order to write formal expressions for the concentrations we shall now introduce some notation.

We define the concentration of vacant silver ion sites by

$$c_v = \frac{N}{B_v} \quad (1.8)$$

and the concentration of interstitials by

$$c_I = \frac{N}{B_I} \quad (1.9)$$

For the crystal structure under consideration (see Fig. 1)

$$B_I = 2 B_v \quad (1.10)$$

so that

$$c_V = 2 c_I. \quad (1.11)$$

Note that c_V will also be the concentration of Frenkel defect pairs. If we ignore defect-defect interactions we rewrite equation (1.6) as

$$c_{V0} = \sqrt{2} \exp (-g_f/2 k T) \quad (1.12)$$

and if we include defect-defect interactions we write

$$c_V = \sqrt{2} \exp [-(g_f - \Delta g)/2 k T], \quad (1.13)$$

where Δg is the change in the free energy of formation due to defect-defect interactions.

The resemblance between ionic crystals and ionic solutions suggests a method for calculating Δg . The interaction among defects in an ionic crystal is similar to that among ions in a solution because at distances greater than a few ionic diameters the interaction may be considered as Coulombic with the properties of the solvent (or host) appearing only via a dielectric constant. For small separations it is no longer valid to speak of a bulk dielectric constant and the discrete nature of the lattice becomes important so that the analogy fails at high defect concentrations. This Debye-Hückel approach considers the vacancies as effectively negative charges and the interstitials as effectively positive charges. These charged defects are dissolved in the silver halide which is considered to be a uniform dielectric with dielectric constant D . The Poisson equation can then be

solved for this system. For $\Delta g \ll kT$ the solution is (Fowler and Guggenheim 1949, p.391)

$$\frac{\Delta g}{2kT} = - \sqrt{\pi c_v} \left(\frac{e^2}{ADkT} \right)^{3/2}, \quad (1.14)$$

where A is the anion-cation separation and e the magnitude of the electronic charge.

Lidiard (1954) improved the Debye-Hückel approach by assuming that oppositely charged nearest neighbor defect pairs were to a good approximation non interacting dipoles. His results have been used to interpret experimental data for such experiments as measurements of ionic conductivity (Allnatt and Jacobs 1962) and of diffusion (Hanlon 1960).

The Debye-Hückel approach even as modified by Lidiard is not adequate in the case of high defect concentrations. A method allowing for the discrete nature of the lattice and making no assumptions about possible defect configurations has been developed by Allnatt and Cohen (1964a; 1964b). They employ the cluster expansion techniques of statistical mechanics (McMillan and Mayer 1945) to obtain formal expressions for the defect concentrations. By applying their formalism to sodium chloride they showed that at high concentrations the result of Lidiard is the first order term in a slowly converging series.

We apply the Allnatt and Cohen formalism to intrinsic cationic Frenkel disorder in the silver halides making a detailed calculation for the particular case of silver

chloride. We calculate the equilibrium concentration of Frenkel defects over the temperature range 400° to 750°K . We then are able to calculate Δg for the same region and compare it to equation (1.14). We perform the calculation for a variety of input parameters. For example, we use both a temperature dependent and temperature independent dielectric constant and compare the results.

II. THEORY

A. Model

Our model of the crystal is an array of point ions arranged in the sodium chloride structure. The chloride ions are fixed to their lattice sites but the silver ions are allowed to leave the cation sublattice to take up interstitial positions. In Fig. 1 we indicate that there are two interstitial sites for every cation site. We give the defect sites labels in the unit cell. The cation site is labeled 1 and the two possible interstitial sites are labeled 2 and 3. The defects then are either vacancies at the cation sites or silver ions at the interstitial sites.

At all separations the defects are considered as interacting with each other via a two body Coulomb interaction assuming the dielectric constant to be that of the bulk crystal. We assume that the nearest neighbor configuration of a silver interstitial and a silver vacancy does not occur because the two defects will annihilate in this configuration. This assumption will be discussed at some length later. Since we assume that the crystal is infinite in extent, the interior of the crystal is electrically neutral and surface effects (Kliewer 1966) can be ignored.

Any macroscopic volume of the crystal interior has a constant number of particles and is in thermal equilibrium with its surroundings so that it is appropriate to work with the canonical ensemble. It is also convenient to work with

the Helmholtz free energy F_H rather than the Gibbs free energy G . Consequently we assume the external pressure on the volume is small so that

$$pV \ll G, \quad (2.1)$$

where p is the external pressure on the macroscopic volume V . Thus we have

$$G = F_H - pV \approx F_H. \quad (2.2)$$

The equilibrium condition then is

$$\frac{\partial F}{\partial N} = 0. \quad (2.3)$$

Our treatment of this model is based on the general formalism developed by Allnatt and Cohen (1964a; 1964b). We follow their treatment closely in many places; the essential difference in treatment lies in the particular application to intrinsic cationic Frenkel disorder.

B. Linked Cluster Expansion of the Partition Function

We will write down the partition function for a canonical ensemble of systems and separate out the part which depends only on the configuration of the vacancy and interstitial defects.

Let N_V be the number of silver ion vacancies in the crystal and N_I be the number of interstitial silver ions. N_V and N_I must be equal to guarantee electrical neutrality

$$N_V = N_I = N, \quad (2.4)$$

where N is the number of defect pairs. The partition function for a canonical ensemble of systems of volume V at temperature T is

$$Q(V, T; N_V + N_I) = \sum_{\{N_V + N_I\}}^1 \sum_i \frac{\exp[-E_i(V, \{N_V + N_I\})/kT]}{N_V! N_I!}. \quad (2.5)$$

The E_i are eigenvalues for the whole crystal in which the defects are in the configuration $\{N_V + N_I\}$, where $\{N_V + N_I\}$ denotes the sites in the crystal occupied by the N_V cation vacancies and the N_I interstitial silver ions. The sum on i is the sum over the vibrational states associated with the thermal energy of the crystal. The factorials appear in the denominator because in the first summation, over all possible configurations of the $N_V + N_I$ defects, the defects are treated as distinguishable. The prime on the summation means that no two defects may simultaneously occupy the same site.

If we consider any particular configuration we can write

$$\sum_i E_i(V, \{N_V + N_I\}) = F_H(V, T; \{N_V + N_I\}), \quad (2.6)$$

where $F_H(V, T; \{N_V + N_I\})$ is the Helmholtz free energy of the system in the particular configuration considered. We write this Helmholtz free energy as a sum of three parts,

$$F_H(V, T; \{N_V + N_I\}) = F_0 + F(N_V + N_I) + F(\{N_V + N_I\}), \quad (2.7)$$

where F_0 is the Helmholtz free energy of the perfect crystal formed by placing the silver interstitials in the cation vacancies, $F(N_V + N_I)$ is the part of the free energy of the

crystal containing defects which depends on the number but not on the configuration of the defects, and $F(\{N_V+N_I\})$ is the part of the free energy which depends on the configuration of the defects. An alternative way to say this is that $F(N_V+N_I)$ is the free energy of formation of the N Frenkel defect pairs with no defect-defect interactions and $F(\{N_V+N_I\})$ is the free energy of interaction of the defects. For brevity let $B = -1/kT$ and $F = F(N_V+N_I)$.

The separation of the Helmholtz free energy leads to a factorization of the partition function

$$Q(V,T; N_V+N_I) = Q_O Q_C, \quad (2.8)$$

where

$$Q_O = \exp B[F_O + F(N_V+N_I)] \quad (2.9)$$

and

$$Q_C = \sum_{\{N_V+N_I\}}^1 \frac{\exp(BF)}{N_V! N_I!}. \quad (2.10)$$

We now factor Q_C into two parts

$$Q_C = Q_C^O Q_C^1, \quad (2.11)$$

where

$$Q_C^O = \frac{B_V!}{N_V! (B_V - N_V)!} \frac{B_I!}{N_I! (B_I - N_I)!} \quad (2.12)$$

and

$$Q_C^1 = \frac{(B_V - N_V)!}{B_V!} \frac{(B_I - N_I)!}{B_I!} \sum_{\{N_V+N_I\}}^1 \exp(BF). \quad (2.13)$$

We will work with Q_c^0 now and return to Q_c^1 later.

For our model F is a sum over the Coulomb interactions between all possible pairs i and j belonging to the set of defects $N_V + N_I$. Now

$$F = \sum_{i,j \in (N_V + N_I)} F_{ij} = \sum_{i,j \in (N_V + N_I)} \frac{Z_i Z_j e^2}{DR_{ij}}, \quad (2.14)$$

with $F_{jj} = 0$, where $Z_i e$ is the charge on defect i and R_{ij} is the distance between defects i and j . F does not include the configurational entropy. The configurational entropy is implicit in Q_c . To see this set $F = 0$ in equation (2.10) to obtain upon summation $\exp(S_{cf}/k)$, where S_{cf} is the configurational entropy. This is in fact factored out in equation (2.11) since S_{cf} is given by $k \log Q_c^0$, Q_c^0 being defined in equation (2.12).

The prime on the summation in equation (2.13) can be removed by employing the Kronecker delta to write

$$\sum_{\{N_V + N_I\}}^1 \exp(BF) = \sum_{\{N_V + N_I\}} \exp(BF) \prod_{i,j \in N_V} (1 - \delta_{ij}) \prod_{k,l \in N_I} (1 - \delta_{kl}) \quad (2.15)$$

where $\prod_{i,j \in N_V}$ is a product over all possible pairs of defects belonging to N_V and $\prod_{k,l \in N_I}$ is defined in an analogous manner. Equation (2.13) then becomes

$$Q_c^1 = \frac{(B_V - N_V)! (B_I - N_I)!}{B_V! B_I!} \sum_{\{N_V + N_I\}} \exp(BF) \prod_{i,j \in N_V} (1 - \delta_{ij}) \prod_{k,l \in N_I} (1 - \delta_{kl}) \quad (2.16)$$

This we abbreviate as

$$Q_c^1 = \langle \exp(BF) \rangle, \quad (2.17)$$

the brackets implying the averaging procedure defined in equation (2.16).

We now expand the exponential in equation (2.17) to get

$$Q_c^1 = 1 + \frac{B\langle F \rangle}{1!} + \frac{B^2\langle F^2 \rangle}{2!} + \dots = \sum_{r=0}^{\infty} \frac{B^r}{r!} \langle F^r \rangle. \quad (2.18)$$

It is convenient to expand $\log Q_c^1$ as a power series in B , that is,

$$\log Q_c^1 = \sum_{n=1}^{\infty} \frac{M_n B^n}{n!}. \quad (2.19)$$

If we make use of the expansion

$$\log(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \quad (2.20)$$

we can equate the right hand sides of equations (2.18) and (2.19) to find the M_n . From equations (2.18) and (2.20) we have

$$\begin{aligned} \log Q_c^1 &= \log \left[1 + \frac{B\langle F \rangle}{1!} + \frac{B^2\langle F^2 \rangle}{2!} + \frac{B^3\langle F^3 \rangle}{3!} + \dots \right] \\ &= \frac{B\langle F \rangle}{1!} + \frac{B^2\langle F^2 \rangle}{2!} - \frac{(B\langle F \rangle)^2}{2} + \frac{B^3\langle F^3 \rangle}{3!} - \frac{B\langle F \rangle B^2\langle F^2 \rangle}{2} + \\ &\quad \frac{(B\langle F \rangle)^3}{3} + \dots \end{aligned} \quad (2.21)$$

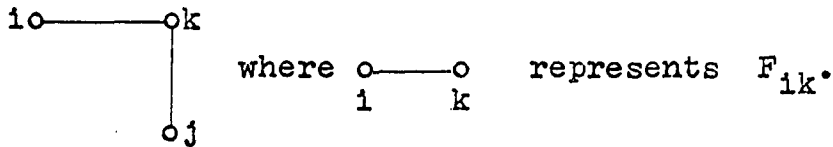
Matching powers of B in equation (2.19) to those in equation (2.21) gives at once

$$\begin{aligned} M_1 &= \langle F \rangle \\ M_2 &= \langle F^2 \rangle - \langle F \rangle^2 \\ M_3 &= \langle F^3 \rangle - 3\langle F \rangle \langle F^2 \rangle + 2\langle F \rangle^3. \end{aligned} \quad (2.22)$$

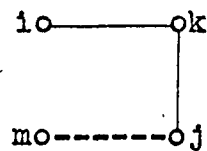
In M_n always occurs

$$\langle F^n \rangle = \frac{(B_V - N_V)! (B_I - N_I)!}{B_V! B_I!} \sum_{\{N_V + N_I\}} F^n \prod_{i,j \in N_V} (1 - \delta_{ij}) \prod_{k,l \in N_I} (1 - \delta_{kl}). \quad (2.23)$$

Each term in the expansion of the right hand side of equation (2.23) can be represented by a diagram. The product $F_{ik} F_{kj}$, for example, is represented by this diagram:

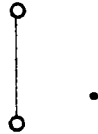


If the Kronecker delta occurs in a product it is represented by a dashed line called a δ bond; for example, the product $F_{ik} F_{kj} \delta_{jm}$ is represented by this diagram:



We shall now classify the different types of diagrams which can occur. Examples of the three different types are drawn in Fig. 2. A diagram is called linked reducible if it can be separated into two or more diagrams by cutting at any vertex. A diagram is called unlinked if it can be

separated into two or more parts unlinked by any bonds. A diagram is called linked irreducible if every node is multiply connected. Two nodes are said to be multiply connected when they are connected by more than one path. In this last type we include also the special case of a single line between two vertices:



Terms corresponding to these first two diagram types can be factored into products of two or more independent summations. To see why this occurs consider diagrams not involving \mathcal{S} bonds. Consider

$$M_2 = \sum_{i,j,k,l} [\langle F_{ij} F_{kl} \rangle - \langle F_{ij} \rangle \langle F_{kl} \rangle] \quad (2.24)$$

in which the following three types of terms occur: no indices in common, one index in common, and two indices in common. We will now show that

$$\langle F_{12} F_{34} \rangle = \langle F_{12} \rangle \langle F_{34} \rangle, \quad (2.25)$$

which is diagrammed

$$\begin{array}{ccc} 1 \circ & \text{---} & \circ 2 \\ & & \\ 3 \circ & \text{---} & \circ 4 \end{array} = \begin{array}{ccc} 1 \circ & \text{---} & \circ 2 \\ & & \\ 3 \circ & \text{---} & \circ 4 \end{array},$$

and

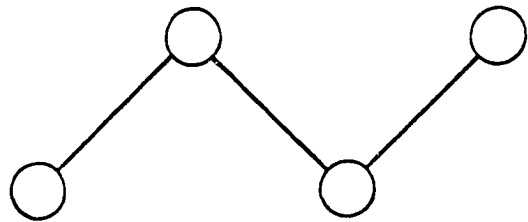
$$\langle F_{12} F_{23} \rangle = \langle F_{12} \rangle \langle F_{23} \rangle \quad (2.26)$$

which is diagrammed

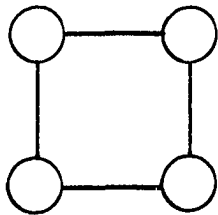
$$\begin{array}{ccccc} 1 & & 2 & & 3 \\ \circ & \text{---} & \circ & \text{---} & \circ \end{array} = \begin{array}{ccccc} 1 & & 2 & & 2 & & 3 \\ \circ & \text{---} & \circ & & \circ & \text{---} & \circ \end{array}.$$



Unlinked



Linked reducible



Linked irreducible

Fig. 2. Diagram classifications

The corresponding diagrams for the left hand sides of equations (2.25) and (2.26) are unlinked and linked reducible, respectively.

Now by definition

$$\langle F_{12} F_{34} \rangle = \frac{(B_V - N_V)! (B_I - N_I)!}{B_V! B_I!} \sum_{\{N_V + N_I\}} F_{12} F_{34}. \quad (2.27)$$

Since

$$\sum_{\{N_V + N_I\}} 1 = \frac{B_V!}{(B_V - N_V)!} \frac{B_I!}{(B_I - N_I)!}. \quad (2.28)$$

we can rewrite equation (2.27) as

$$\langle F_{12} F_{34} \rangle = \left[\frac{(B_V - N_V)! (B_I - N_I)!}{B_V! B_I!} \right]^2 \sum_{\{N_V + N_I\}} \sum_{\{N_V + N_I\}} F_{12} F_{34}. \quad (2.29)$$

Now F_{12} is independent of particles 3 and 4 so we have

$$\langle F_{12} F_{34} \rangle = \left[\frac{(B_V - N_V)! (B_I - N_I)!}{B_V! B_I!} \sum_{\{N_V + N_I\}} F_{12} \right] \left[\frac{(B_V - N_V)! (B_I - N_I)!}{B_V! B_I!} \sum_{\{N_V + N_I\}} F_{34} \right] \quad (2.30)$$

which is a restatement of equation (2.25)

Turning to the proof of equation (2.26) we have by definition

$$\langle F_{12} F_{23} \rangle = \frac{(B_V - N_V)! (B_I - N_I)!}{B_V! B_I!} \sum_{\{N_V + N_I\}} F_{12} F_{23}. \quad (2.31)$$

Since F_{12} is not independent of particle 2 which appears

in F_{23} we cannot proceed as we did in the proof of equation (2.25). However, we can still write

$$\langle F_{12} F_{23} \rangle = \left[\frac{(B_V - N_V)!}{B_V!} \frac{(B_I - N_I)!}{B_I!} \right]^2 \sum_{\{N_V + N_I\}} \sum_{\{N_V + N_I\}} F_{12} F_{23}. \quad (2.32)$$

Recall that F_{ij} equals $Z_i Z_j e^2 / DR_{ij}$ and redefine the origin for R in the second summation in equation (2.32) so that it coincides with particle 2. We can then write

$$\langle F_{12} F_{23} \rangle = \frac{(B_V - N_V)!}{B_V!} \frac{(B_I - N_I)!}{B_I!} \sum_{\{N_V + N_I\}} F_{12} \frac{(B_V - N_V)!}{B_V!} \frac{(B_I - N_I)!}{B_I!} \sum_{\{N_V + N_I\}} F_{23}, \quad (2.33)$$

which is equivalent to equation (2.26). For general M_n we can proceed in similar fashion.

Application of equations (2.25) and (2.26) to equation (2.24) shows that contributions to M_2 always vanish when $\langle F_{ij} F_{kl} \rangle$ corresponds to an unlinked or linked reducible diagram. This is similarly true for arbitrary M_n . Only when the leading term corresponds to an irreducible diagram do we have a contribution to M_n . For example, M_2 has a non-vanishing contribution from

$$\langle F_{12}^2 \rangle - \langle F_{12} \rangle^2, \quad (2.34)$$

but by the definition of the averaging process implied by the brackets the second term in expression (2.34) is negligible compared to the first.

To see that $\langle F_{12} \rangle^2 \ll \langle F_{12}^2 \rangle$ (2.35)

we employ equation (2.23) to find

$$\frac{\langle F_{12} \rangle^2}{\langle F_{12}^2 \rangle} = \frac{(B_V - N_V)!}{(B_V - 1)!} \frac{(B_I - N_I)!}{B_I!} \frac{(\sum_{\{2\}} F_{12})^2}{\sum_{\{2\}} (F_{12}^2)}, \quad (2.36)$$

where we have assumed (with no loss of generality for our argument) that defect 1 is a vacancy and defect 2 is an interstitial. Now

$$\sum_{\{2\}} F_{12} \leq \frac{Z_1 Z_2 e^2}{DA} B_I \quad (2.37)$$

so that

$$\frac{\langle F_{12} \rangle^2}{\langle F_{12}^2 \rangle} \leq \frac{(B_V - N_V)!}{(B_V - 1)!} \frac{(B_I - N_I)!}{(B_I - 2)!} \frac{1}{A^2 \sum_{\{2\}} R_{12}^{-2}} \leq \frac{(B_V - N_V)!}{(B_V - 1)!} \frac{(B_I - N_I)!}{(B_I - 2)!} \ll 1. \quad (2.38)$$

Now we have a rule for writing down all the contributions to M_n . They are the terms corresponding to all irreducibly linked diagrams containing n bonds among p vertices where $2 \leq p \leq n$. The combinatorial factor for a diagram with p vertices is the product of 2 binomial coefficients, $\binom{N_V}{p_V} \binom{N_I}{p_I}$ where p_V is the number of vertices representing vacancies and p_I is the number of vertices representing interstitials. Clearly

$$p_V + p_I = p. \quad (2.39)$$

This is the correct combinatorial factor because we want it to be given by

$$\begin{aligned}
 & \left(\begin{array}{l} \text{number of ways to pick } P_V \\ \text{indistinguishable vacancies} \\ \text{from the set of } N_V \\ \text{vacancies} \end{array} \right) \times \left(\begin{array}{l} \text{number of ways to pick } P_I \\ \text{indistinguishable inter-} \\ \text{stitials from the set of} \\ N_I \text{ vacancies} \end{array} \right) \\
 &= \frac{(N_V(N_V-1)\cdots(N_V-P_V+1))}{P_V!} \times \frac{N_I(N_I-1)\cdots(N_I-P_I+1)}{P_I!} \\
 &= \frac{N_V!}{(N_V-P_V)!P_V!} \frac{N_I!}{(N_I-P_I)!P_I!} = \binom{N_V}{P_V} \binom{N_I}{P_I} . \quad (2.40)
 \end{aligned}$$

To clarify what is meant by p , p_V , and p_I consider the case for $p=2$. We would then write

$$p_V = 2_V$$

and

$$p_I = 2_I$$

(2.41)

so that $p_V + p_I = 2_V + 2_I = 2$. The possible values for the pair $(2_V, 2_I)$ would be $(2,0)$, $(1,1)$, and $(0,2)$.

To obtain $\log Q_c^1$ it is instructive to consider the contributions from the set of diagrams with two vertices and then from the set of diagrams with three vertices. Recall that we are still ignoring the \mathcal{S} bonds. The contribution to $\log Q_c^1$ from the set of diagrams with two vertices labeled 1 and 2 is

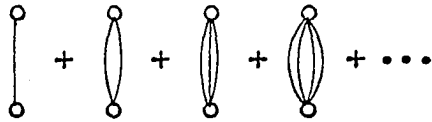
$$\binom{N_V}{2_V} \binom{N_I}{2_I} \sum_{n=1}^{\infty} \frac{B_{12}^{nF} n}{n!} = \binom{N_V}{2_V} \binom{N_I}{2_I} \langle e^{B_{12}^{BF} - 1} \rangle$$

$$\begin{aligned}
&= \binom{N_V}{2_V} \binom{N_I}{2_I} \frac{(B_V - N_V)!}{B_V!} \frac{(B_I - N_I)!}{B_I!} \sum_{\{N_V + N_I\}} (e^{BF_{12} - 1}) \\
&= \binom{N_V}{2_V} \binom{N_I}{2_I} \frac{(B_V - N_V)!}{(B_V - N_V + 2_V)!} \frac{(B_I - N_I)!}{(B_I - N_I + 2_I)!} \sum_{\{1,2\}} (e^{BF_{12} - 1}) \\
&- \left(\frac{N_V}{B_V} \right)^{2_V} \left(\frac{N_I}{B_I} \right)^{2_I} \frac{1}{2_V! 2_I!} \sum_{\{1,2\}} (e^{BF_{12} - 1}), \tag{2.42}
\end{aligned}$$

where use has been made of the conditions

$$\begin{aligned}
2_V < B_V - N_V & \quad 2_V < N_V & \quad N_V < B_V \\
2_I < B_I - N_I & \quad 2_I < N_I & \quad N_I < B_I
\end{aligned} \tag{2.43}$$

Diagrammatically the left hand side of equation (2.42) is given by



The multiply connected nodes occur as a consequence of the expansion in equation (2.18). A pair of multiply connected nodes corresponding to defects physically close together contributes more than a pair corresponding to widely separated defects because the contribution is of form $\frac{(BF_{ij})^n}{n!}$ where n is the number of bonds connecting defects i and j . To include all two vertex diagrams not merely those with vertices labeled 1 and 2 we write

$$\begin{aligned}
&\left(\frac{N_V}{B_V} \right)^{2_V} \left(\frac{N_I}{B_I} \right)^{2_I} \frac{1}{2_V! 2_I!} \left[\sum_{\{I, I\}} (e^{BF_{II} - 1}) + \sum_{\{I, v\}} (e^{BF_{Iv} - 1}) + \right. \\
&\quad \left. \sum_{\{v, I\}} (e^{BF_{vI} - 1}) + \sum_{\{v, v\}} (e^{BF_{vv} - 1}) \right]
\end{aligned}$$

$$\begin{aligned}
&= \left(\frac{N_V}{B_V} \right)^{2_V} \left(\frac{N_I}{B_I} \right)^{2_I} \frac{1}{2_V! 2_I!} \sum_{i=I}^V \sum_{j=I}^V \sum_{\{i,j\}} (e^{BF_{ij-1}}) \\
&= \left(\frac{N_V}{B_V} \right)^{2_V} \left(\frac{N_I}{B_I} \right)^{2_I} \frac{1}{2_V! 2_I!} \sum_{i,j} \sum_{\{i,j\}} (e^{BF_{ij-1}}), \quad (2.44)
\end{aligned}$$

where $\sum_{\{i,j\}}$ is a sum over distinguishable configurations.

Now we proceed to the contribution to $\log Q_c^1$ from the set of diagrams with three vertices labeled 1, 2, and 3. Let there be s_{12} bonds connecting vertices 1 and 2, s_{23} bonds connecting vertices 2 and 3, and s_{31} bonds connecting vertices 3 and 1.

The number of ways we can arrange n things into three classes such that

$$s_{12} + s_{23} + s_{31} = n \quad (2.45)$$

is

$$\frac{n!}{s_{12}! s_{23}! s_{31}!} \cdot \quad (2.46)$$

The contribution to $\log Q_c^1$ is

$$\begin{aligned}
&\left(\frac{N_V}{3_V} \right) \left(\frac{N_I}{3_I} \right) \sum_{n=3}^{\infty} \sum_{\substack{s_{12}, s_{23}, s_{31}=1 \\ s_{12}+s_{23}+s_{31}=n}}^{\infty} \frac{B^n}{n!} \frac{n!}{s_{12}! s_{23}! s_{31}!} \\
&\quad < F_{12}^{s_{12}} F_{23}^{s_{23}} F_{31}^{s_{31}} > \\
&= \left(\frac{N}{3_V} \right) \left(\frac{N_I}{3_I} \right) < \sum_{s_{12}=1}^{\infty} \frac{(BF_{12})^{s_{12}}}{s_{12}!} \sum_{s_{23}=1}^{\infty} \frac{(BF_{23})^{s_{23}}}{s_{23}!} \sum_{s_{31}=1}^{\infty} \frac{(BF_{31})^{s_{31}}}{s_{31}!} >
\end{aligned}$$

$$\begin{aligned}
&= \binom{N}{3_V} \binom{N_I}{3_I} \langle (e^{BF_{12}-1})(e^{BF_{23}-1})(e^{BF_{31}-1}) \rangle \\
&= \binom{N_V}{3_V} \binom{N_I}{3_I} \frac{(B_V - N_V)!}{(B_V - N_V + 3_V)!} \frac{(B_I - N_I)!}{(B_I - N_I + 3_I)!} \sum_{\{1,2,3\}} (e^{BF_{12}-1})(e^{BF_{23}-1}) \\
&\quad (e^{BF_{31}-1}) \\
&- \left(\frac{N_V}{B_V} \right)^{3_V} \left(\frac{N_I}{B_I} \right)^{3_I} \frac{1}{3_V! 3_I!} \sum_{\{1,2,3\}} (e^{BF_{12}-1})(e^{BF_{23}-1})(e^{BF_{31}-1}).
\end{aligned} \tag{2.47}$$

The last step in equation (2.47) follows from the inequalities

$$\begin{aligned}
3_V &< B_V - N_V \\
3_I &< B_I - N_I \\
3_V &< N_V \\
3_I &< N_I \\
N_V &< B_V \\
N_I &< B_I.
\end{aligned} \tag{2.48}$$

To include all three vertex diagrams not just those with vertices labeled 1, 2, and 3 we write

$$\begin{aligned}
&\left(\frac{N_V}{B_V} \right)^{3_V} \left(\frac{N_I}{B_I} \right)^{3_I} \frac{1}{3_V! 3_I!} \sum_{i,j,k} \sum_{\{1,j,k\}} (e^{BF_{1j}-1})(e^{BF_{jk}-1}) \\
&\quad (e^{BF_{ki}-1}).
\end{aligned} \tag{2.49}$$

To obtain the terms contributing to $\log Q_c^1$ corresponding to higher numbers of vertices than three, we proceed as we did to get the expressions (2.44) and (2.49). We then add

up all these contributions to get the total contribution to $\log Q_c^1$ from terms not containing δ bonds. This is

$$\sum_{p \geq 2} \left(\frac{N_V}{B_V} \right)^{P_V} \left(\frac{N_I}{B_I} \right)^{P_I} \frac{1}{P_V! P_I!} \sum_{\{p\}} \sum \prod (e^{BF_{ij-1}}), \quad (2.50)$$

where the meaning of the symbols $\sum \sum \prod_{\{p\}}$ is evident upon comparison with the expressions (2.44) and (2.49). Recall also that $p_V + p_I = p$. Let the set p consist of defects 1, 2, 3, ..., p which may be vacancies, v , or interstitials, I . Thus

$$\sum_{\{p\}} \sum \prod = \sum_{\{1, \dots, p\}} \left[\sum_{l=I_1}^{v_1} \sum_{2=I_2}^{v_2} \dots \sum_{p=I_p}^{v_p} \left(\prod_{i,j \in p} (e^{BF_{ij-1}}) \right) \right]. \quad (2.51)$$

We must now include the δ bonds. Recall that δ bonds may only link directly vertices corresponding to defects on the same sublattice. We also see from equation (2.16) that only a single δ bond can link directly any pair of vertices. Consider a diagram with n F bonds distributed among p vertices. Corresponding to this diagram there is the set of all diagrams which can be formed from it by adding δ bonds among the p vertices.

Further, there are all the diagrams which can be formed from each diagram of this new set and from the original diagram by first adding any number of new vertices corresponding to the defects not represented already and then adding δ bonds so that every vertex is directly connected to at

least one other vertex. All the new diagrams will give zero contribution to $\log Q_c^1$ except those which are irreducibly linked because of the factorization property of the summations involved. Also, all diagrams in which a δ bond or δ bond chain and at least one F bond connect the same pair of vertices will give zero contribution because

$$\delta_{ij} F_{ij} = F_{jj} = 0$$

and

$$\delta_{ik} \delta_{kl} \delta_{lj} F_{ij} = \delta_{ij} F_{ij} = F_{jj} = 0. \quad (2.52)$$

The contributions of the nonvanishing irreducible diagrams may be summed exactly as for the case of F bonds only.

For example, consider $p = 3$ and refer to equation (2.47) which we modify by letting $S_{31} = 0$ and replacing $F_{31}^{S_{31}}$ by $-\delta_{31}$. Proceeding as in equation (2.47) we obtain

$$\begin{aligned} & \binom{N_V}{3_V} \binom{N_I}{3_I} \sum_{n=2} \sum_{\substack{s_{12}, s_{23}=1 \\ s_{12}+s_{23}=n}} \frac{B^n}{n!} \frac{n!}{s_{12}! s_{23}!} \langle F_{12}^{s_{12}} F_{23}^{s_{23}} (-\delta_{31}) \rangle \\ &= \left(\frac{N_V}{B_V} \right)^{3_V} \left(\frac{N_I}{B_I} \right)^{3_I} \frac{1}{3_V! 3_I!} \sum_{\{1,2,3\}} (e^{BF_{12}-1}) (e^{BF_{23}-1}) (-\delta_{31}). \end{aligned} \quad (2.53)$$

Combining equations (2.47) and (2.53) yields

$$\begin{aligned} & \left(\frac{N_V}{B_V} \right)^{3_V} \left(\frac{N_I}{B_I} \right)^{3_I} \frac{1}{3_V! 3_I!} \sum_{\{1,2,3\}} (e^{BF_{12}-1}) (e^{BF_{23}-1}) (e^{BF_{31}-1} - \delta_{31}). \end{aligned} \quad (2.54)$$

Before we write $\log Q_c^1$ we wish to rewrite $\log Q_c^0$.

From equation (2.12) we have

$$\begin{aligned}\log Q_c^0 &= \log \left[\frac{B_V!}{N_V!(B_V-N_V)!} \frac{B_I!}{N_I!(B_I-N_I)!} \right] \\ &= \log B_V! + \log B_I! - \log(B_V-N_V)! \\ &\quad - \log(B_I-N_I)! - \log N_V! - \log N_I!. \quad (2.55)\end{aligned}$$

We have already in the inequalities (2.43) and (2.48) assumed that B_V , B_I , N_V , and N_I are large numbers. Hence we employ Stirling's Approximation so that

$$\begin{aligned}\log Q_c^0 &= B_V \log B_V - B_V + B_I \log B_I - B_I \\ &\quad - (B_V - N_V) \log(B_V - N_V) + (B_V - N_V) \\ &\quad - (B_I - N_I) \log(B_I - N_I) + (B_I - N_I) \\ &\quad - N_V \log N_V + N_V - N_I \log N_I + N_I \\ &= \log \left(\frac{B_V - N_V}{B_V} \right)^{N_V - B_V} + \log \left(\frac{B_I - N_I}{B_I} \right)^{N_I - B_I} \\ &\quad - \log \left(\frac{N_V}{B_V} \right)^{N_V} - \log \left(\frac{N_I}{B_I} \right)^{N_I} \\ &= \left[\log(1 - c_V)^{N_V - B_V} - N_V + \log(1 - c_I)^{N_I - B_I} - N_I \right] \\ &\quad - \log \left(\frac{c_V}{e} \right)^{N_V} - \log \left(\frac{c_I}{e} \right)^{N_I}. \quad (2.56)\end{aligned}$$

We shall now show that the term in brackets in equation (2.56) can be written

$$\begin{aligned} \log(1-c_V)^{N_V-B_V} - N_V + \log(1-c_I)^{N_I-B_I} - N_I \\ = \sum_{p \geq 2} \frac{c_V^p}{p_V!} \frac{c_I^p}{p_I!} \sum_{\{p\}} (\sum_p \Pi(-\delta_{1j})) \end{aligned} \quad (2.57)$$

where the symbols $\sum \sum_p \Pi$ are those of equation (2.51). Note that by our definition of the δ bonds equation (2.57) vanishes unless all the vertices correspond to defects on the same sublattice. Hence the right hand side of equation (2.57) can be written

$$\sum_{p_V \geq 2} \frac{c_V^p}{p_V!} \sum_{\{p_V\}} \Pi(-\delta_{1j}) + \sum_{p_I \geq 2} \frac{c_I^p}{p_I!} \sum_{\{p_I\}} \Pi(-\delta_{1j}). \quad (2.58)$$

There is a theorem (Neville 1953) which states

$$\sum_{p_V} \Pi(-\delta_{1j}) = -B_V(p_V-2)!$$

and

$$\sum_{p_I} \Pi(-\delta_{1j}) = -B_I(p_I-2)! \quad (2.59)$$

Using expression (2.58) and equations (2.59) the right hand side of equation (2.57) becomes

$$- \sum_{p_V \geq 2} \frac{c_V^p}{p_V(p_V-1)} B_V - \sum_{p_I \geq 2} \frac{c_I^p}{p_I(p_I-1)} B_I. \quad (2.60)$$

To match the left hand side of equation (2.57) to expression (2.60) we note that

$$\begin{aligned}
 \log(1-c_I)^{N_I-B_I} - N_I &= (N_I-B_I)\log(1-c_I) - B_I c_I \\
 &= B_I(1-c_I) \sum_{p_I=1}^{\infty} \frac{c_I^{p_I}}{p_I} - B_I c_I = B_I \sum_{p_I=1}^{\infty} \frac{c_I^{p_I}}{p_I} - B_I \sum_{p_I=1}^{\infty} \frac{c_I^{p_I+1}}{p_I} - B_I c_I \\
 &= B_I c_I + B_I \left[\sum_{p_I=2}^{\infty} \frac{c_I^{p_I}}{p_I} - \sum_{p_I=2}^{\infty} \frac{c_I^{p_I}}{p_I-1} \right] - B_I c_I \\
 &= -B_I \sum_{p_I \geq 2} \frac{c_I^{p_I}}{p_I(p_I-1)} \tag{2.61}
 \end{aligned}$$

and similarly

$$\log(1-c_V)^{N_V-B_V} - N_V = -B_V \sum_{p_V \geq 2} \frac{c_V^{p_V}}{p_V(p_V-1)}. \tag{2.62}$$

Thus equation (2.57) is verified and we now have

$$\log Q_c^0 = \sum_{p \geq 2} \frac{c_V^{p_V}}{p_V!} \frac{c_I^{p_I}}{p_I!} \sum_{\{p\}} (\sum \mathcal{L}(-\delta_{1j})) - \log \left(\frac{c_V}{e} \right)^{N_V} - \log \left(\frac{c_I}{e} \right)^{N_I}. \tag{2.63}$$

From equation (2.63) and expression (2.50) with its following discussion we obtain

$$\begin{aligned}
 \log Q_c &= \sum_{p \geq 2} \frac{c_V^{p_V}}{p_V!} \frac{c_I^{p_I}}{p_I!} \sum_{\{p\}} (\sum \mathcal{L}(e^{BF_{1j}-1-\delta_{1j}})) - \log \left(\frac{c_V}{e} \right)^{N_V} \\
 &\quad - \log \left(\frac{c_I}{e} \right)^{N_I}. \tag{2.64}
 \end{aligned}$$

This is the linked cluster expansion of the partition function. We reiterate that δ bonds link only vertices corresponding to defects on the same sublattice and that all diagrams in which a pair of vertices are directly linked by at least one F bond and by a δ bond or δ bond chain, give zero contribution to $\log Q_c$.

C. Activity Coefficients

1. Definition of activity coefficients

The condition for equilibrium given in equation (2.3) gives for Frenkel disorder

$$(dF_H)_{T,V} = \left. \frac{\partial F_H}{\partial N_V} \right|_{T,V} dN_V + \left. \frac{\partial F_H}{\partial N_I} \right|_{T,V} dN_I = 0. \quad (2.65)$$

Electrical neutrality demands that

$$dN_V - dN_I = 0. \quad (2.66)$$

We define chemical potentials by

$$\mu_V = \left. \frac{\partial F_H}{\partial N_V} \right|_{T,V} \quad (2.67)$$

and

$$\mu_I = \left. \frac{\partial F_H}{\partial N_I} \right|_{T,V} \quad (2.68)$$

Substitution of equations (2.66), (2.67), and (2.68) into equation (2.65) gives

$$\mu_V + \mu_I = 0. \quad (2.69)$$

From equations (2.67), (2.7), (2.10), and (2.64) we have

$$\begin{aligned} \mu_v = & \frac{F(N_v + N_I)}{N_v} + k T \log c_v \\ & - k T \frac{1}{B_v} \frac{\partial}{\partial c_v} \sum_{p \geq 2} \frac{c_v^{p_v}}{p_v!} \frac{c_I^{p_I}}{p_I!} \sum_{\{p\}} (\sum \pi f_{ij}), \end{aligned} \quad (2.70)$$

where

$$f_{ij} = e^{BF_{ij}} - 1 - \delta_{ij}. \quad (2.71)$$

We rewrite equation (2.70) as

$$\mu_v = F_v + k T \log(c_v \gamma_v), \quad (2.72)$$

where

$$F_v = \frac{F(N_v + N_I)}{N_v} \quad (2.73)$$

is the change in the Helmholtz free energy on adding a non-interacting silver vacancy to the crystal at constant T and V and

$$\log \gamma_v = - \frac{1}{B_v} \frac{\partial}{\partial c_v} \sum_{p \geq 2} \frac{c_v^{p_v} c_I^{p_I}}{p_v! p_I!} \sum_{\{p\}} (\sum \pi f_{ij}) \quad (2.74)$$

defines the vacancy activity coefficient, γ_v . In an analogous fashion we have

$$\mu_I = F_I + k T \log(c_I \gamma_I), \quad (2.75)$$

where F_I is the change in the Helmholtz free energy on adding an interstitial silver ion to the crystal at constant T and V and

$$\log \gamma_I = - \frac{1}{B_I} \frac{\partial}{\partial c_I} \sum_{p \geq 2} \frac{c_V^{p_V} c_I^{p_I}}{p_V! p_I!} \sum_{\{p\}} (\sum \Pi f_{ij}) \quad (2.76)$$

defines the interstitial activity coefficient, γ_I . From equations (2.69), (2.72), and (2.75) it follows that

$$c_V c_I \gamma_V \gamma_I = e^{-(F_V + F_I)/kT}. \quad (2.77)$$

Note that $F_V + F_I$ is just the change in the Helmholtz free energy on adding a Frenkel pair to the crystal. Comparison of equation (2.77) with equation (1.13) shows that

$$\gamma_V \gamma_I = \exp(-\Delta g/kT). \quad (2.78)$$

Our self consistent calculation here is based on equations (2.74), (2.76), and (2.77). Initially we choose reasonable concentrations and substitute these into equations (2.74) and (2.76). The resulting activity coefficients are then substituted into equation (2.77) to get new concentrations. The procedure is repeated until the desired degree of self consistency is achieved.

However, equations (2.74) and (2.76) are not yet in forms from which we can get numerical results. The rest of this section is devoted to obtaining such forms.

We now introduce symbols which will later prove convenient:

$$R(P) = \Sigma \prod f_{ij} \quad (2.79)$$

and

$$S = \frac{1}{B^*} \Sigma_{p \geq 2} \frac{c_v^p}{p_v!} \frac{c_I^p}{p_I!} \Sigma_{\{p\}} R(P), \quad (2.80)$$

where $B^* = B_v + B_I$. Equations (2.74) and (2.76) become, therefore,

$$\log \gamma_v = - \frac{B^*}{B_v} \frac{\partial S}{\partial c_v} \quad (2.81)$$

and

$$\log \gamma_I = - \frac{B^*}{B_I} \frac{\partial S}{\partial c_I}. \quad (2.82)$$

We also expand the exponent appearing in f_{ij} so that

$$f_{ij} = e^{BF_{ij}} - 1 - \delta_{ij} = -\delta_{ij} + \Sigma_{n \geq 1} \frac{(-Z_i Z_j \lambda q_{ij})^n}{n!} \quad (2.83)$$

$$\text{where } \lambda = \frac{4\pi e^2}{DkT} \quad (2.84)$$

$$\text{and } q_{ij} = \frac{1}{4\pi R_{ij}} \quad (2.85)$$

We then have upon substitution of equation (2.83) into (2.80)

$$R(p) = \Sigma \prod \left(-\delta_{ij} + \Sigma_{n \geq 1} \frac{(-Z_i Z_j \lambda q_{ij})^n}{n!} \right). \quad (2.86)$$

Each product in $R(p)$ can be diagrammed. Let us retain our earlier definition of δ bonds as dashed lines but now let solid lines represent q bonds. For example, a typical

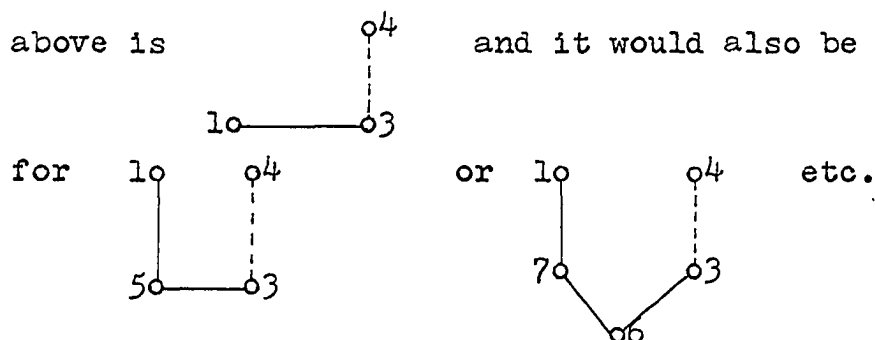
product in the summand would be

$$\begin{array}{c} 10 \\ | \\ 20 \end{array} \begin{array}{c} 04 \\ \vdots \\ 03 \end{array} \quad \text{representing} \quad \frac{(-Z_1 Z_2 \lambda q_{12})}{1} \frac{(-Z_2 Z_3 \lambda q_{23})}{1} \delta_{34}. \quad (2.87)$$

A q bond chain is defined as a row of vertices each connected to the preceding one and to the following one by a single direct q bond and connected to no other vertex.

In our example above there is a q bond chain connecting vertex 3. δ bond chains are similarly defined.

Diagrams containing no q bond chains are called prototype diagrams and from these all other diagrams can be derived by replacing some or all of the q bonds in the prototype by q bond chains. The prototype for our example above is



Assume that we can uniquely describe a diagram with p vertices by a set of symbols, $\tau(p)$, which we call a pattern. Patterns corresponding to prototype diagrams are called prototype patterns and are written $\sigma(p)$. For a diagram with p vertices we write

$$\tau(p) = \tau(n+M) = \sigma(m); h(n_1), h(n_2), \dots, h(n), \quad (2.88)$$

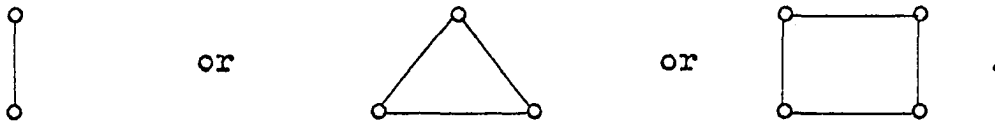
This means that $\tau(p)$ can be derived from a prototype pattern $\sigma(m)$ with $m < p$ by adding n vertices involved

in q bond chains to the prototype. There are ν q bond chains in all and in chain j there are n_j vertices arranged in the order $h(n_j)$. Consider again the example given in relation (2.87). For that case $n=n_1=1$.


The sum of products $R(p)$ is equivalent to the sum of $R[\tau(p)]$ over all possible patterns. Thus we write

$$S = \sum_{p \geq 2} \frac{c_v^{p_v} c_I^{p_I}}{p_v! p_I!} \frac{1}{B^*} \sum_{\tau(p)} R[\tau(p)] . \quad (2.89)$$

We separate S into three parts according to their patterns. There is a particular class of patterns defining diagrams which are simple cycles of single q bonds, for example



The contribution of such diagrams to S is written S^c .

Diagrams involving only a single q bond between two vertices give another contribution which we label S^e :  .

Hence, we write $S = S^c + S^e + S^R$ (2.90)

where S^R is the contribution to S from all patterns other than those involved in S^e and S^c . We shall later show that the contribution of S^c is the Debye-Hückel result. The treatment of S^e will suggest a method for treating S^R .

2. Contributions of the cycle diagrams to the activity coefficients

We have for S^c ,

$$S^c = \sum_{p \geq 2} \frac{c_v^{p_v} c_I^{p_I}}{p_v! p_I!} \frac{1}{B^*} \sum_{\{p\}} (\sum \prod (-\lambda q_{ij} Z_i Z_j)). \quad (2.91)$$

Recall that the last summation sign is over every distinguishable arrangement of the vertices where every vertex is labeled and distinguishable. For a given composition the vacancies may be interchanged in $p_v!$ ways and the interstitials in $p_I!$ ways so we have

$$S^c = \sum_{p \geq 2} \frac{c_v^{p_v} c_I^{p_I}}{B^*} \sum_{\{p\}} (\sum^{ll} \prod (-\lambda q_{ij} Z_i Z_j)) \quad (2.92)$$

where \sum^{ll} is a sum over all distinguishable arrangements of a set of vertices of composition p in a cycle, with like defects considered indistinguishable.

In this form S^c does not converge rapidly. Further, it would only be practical to attempt the first two terms in the sum, that is, $p=2$ and $p=3$. To get a usable form for S^c we employ a Fourier transform procedure. First we must introduce some notation. Let defects r and s be in unit cells l and m , respectively. These unit cells are located \vec{R}_l and \vec{R}_m with respect to an arbitrary origin. The positions of r and s within their respective unit cells are given by $\vec{\lambda}_r^{(x)}$ and $\vec{\lambda}_s^{(y)}$. x and y denote

the labeled positions 1, 2, and 3 of Fig. 1. Therefore, the vector from defect r to defect s is

$$\vec{R}_{rs} = \vec{R}_1 - \vec{R}_m + \vec{\lambda}_r^{(x)} - \vec{\lambda}_s^{(y)} \quad (2.93)$$

which we abbreviate by

$$\vec{R}_{rs} = \vec{R}_{lm} + \vec{\lambda}_{rs}^{(xy)} \quad (2.94)$$

Abbreviate $(-\lambda c_r Z_r Z_s c_{rs})$ as $\gamma_{rs}(\vec{R}_{rs})$.

The Fourier transform of $\gamma_{rs}(\vec{R}_{rs})$ is

$$w_{rs}^{(xy)}(\vec{t}) = \sum_{m \neq 1} e^{-i\vec{t} \cdot (\vec{R}_{lm} + \vec{\lambda}_{rs}^{(xy)})} \gamma_{rs}(\vec{R}_{lm} + \vec{\lambda}_{rs}^{(xy)}), \quad (2.95)$$

where \vec{t} is a vector in the first Brillouin zone of the reciprocal space. The inverse of equation (2.95) is

$$\gamma_{rs}(\vec{R}_{rs}) = \frac{\Delta}{(2\pi)^3} \int_{B.Z.} d\vec{t} e^{i\vec{t} \cdot \vec{R}_{rs}} w_{rs}^{(xy)}(\vec{t}), \quad (2.96)$$

where Δ is the volume of the unit cell in real space. The integration is to be carried out over the first Brillouin zone whose volume is $(2\pi)^3/\Delta$. We wish to express S^c in terms of the $w_{ij}^{(xy)}$.

Now define

$$S_{rls}(\vec{R}_{rs}) = \sum_{\{l\}} \gamma_{rl}(\vec{R}_{rl}) \gamma_{ls}(\vec{R}_{ls}), \quad (2.97)$$

where the sum is over each site of defect l on its own sublattice.

The Fourier transform of $S_{rls}(\vec{R}_{rs})$ is

$$\Phi_{rls}^{(xy)} = \sum_{m \neq l} e^{-i\vec{t} \cdot (\vec{R}_{lm} + \vec{\lambda}_{rs})} S_{rls}(\vec{R}_{lm} + \vec{\lambda}_{rs})^{(xy)} \quad (2.98)$$

with an inverse transformation given by

$$S_{rls}(\vec{R}_{rs}) = \frac{\Delta}{(2\pi)^3} \int d\vec{t} e^{i\vec{t} \cdot \vec{R}_{rs}} \Phi_{rls}^{(xy)} \quad (2.99)$$

Substitution of equation (2.87) into equation (2.98) and using equation (2.95) yields

$$\Phi_{rls}^{(xy)} = \sum_a w_{rl}^{(xa)}(\vec{t}) w_{ls}^{(ay)}(\vec{t}), \quad (2.100)$$

where the summation is over all the positions available to defect 1 in a unit cell. For example, if defect 1 were an interstitial

$$\Phi_{rls}^{(xy)} = w_{rl}^{(x2)} w_{ls}^{(2y)} + w_{rl}^{(x3)} w_{ls}^{(3y)} \quad (2.101)$$

This procedure can be repeated for a chain of n defects lying between r and s to find

$$\begin{aligned} S_{rl2\dots ns}(\vec{R}_{rs}) &= \sum_{\{1,2,\dots,n\}} \gamma_{rl}(\vec{R}_{r1}) \gamma_{12}(\vec{R}_{12}) \dots \gamma_{ns}(\vec{R}_{ns}) \\ &= \frac{\Delta}{(2\pi)^3} \int_{B.Z.} d\vec{t} e^{i\vec{t} \cdot \vec{R}_{rs}} \sum_{a,b,\dots,g} w_{rl}^{(xa)}(\vec{t}) w_{12}^{(ab)}(\vec{t}) \dots \\ &\quad w_{ns}^{(gy)}(\vec{t}). \end{aligned} \quad (2.102)$$

To get a cycle instead of a chain of defects define

$$S_{r12\dots ns}^c = \sum_{\{r,1,2,n,s\}} \gamma_{r1}(\vec{R}_{r1}) \gamma_{12}(\vec{R}_{12}) \dots \gamma_{ns}(\vec{R}_{ns}) \gamma_{sr}(\vec{R}_{sr}). \quad (2.103)$$

From equations (2.102) and (2.103) we obtain

$$\begin{aligned} S_{r12\dots ns}^c &= \sum_{\{r\}} S_{r12\dots nsr}(\vec{R}_{rr}) \\ &= \frac{\Delta}{(2\pi)^3} \sum_{\{r\}} \int_{B.Z.} d\vec{t} e^{i\vec{t} \cdot \vec{R}_{rr}} \sum_{a,b,\dots,g,y} \gamma_{r1}^{(xa)}(\vec{t}) \dots \gamma_{ns}^{(gy)}(\vec{t}) \\ &\quad \gamma_{sr}^{(yx)}(\vec{t}) \\ &= \frac{B_v^*}{(2\pi)^3} \int_{B.Z.} d\vec{t} \sum_{x,a,\dots,g,y} [\gamma_{r1}^{(xa)}(\vec{t}) \dots \gamma_{sr}^{(yx)}(\vec{t})], \quad (2.104) \end{aligned}$$

where we have used the facts that $\vec{R}_{rr}=0$ and $\sum_{\{r\}} B_v \sum_x$ where B_v is the number of unit cells and \sum_x is the sum over the positions available to defect r in its own unit cell.

Abbreviate the term in brackets on the right hand side of equation (2.104) as $\sum_{x,y} \Pi_{ij}^{(xy)}(\vec{t})$. Equation (2.104) then

becomes

$$S_{r12\dots ns}^c = \frac{B_v \Delta}{(2\pi)^3} \int_{B.Z.} d\vec{t} \sum_{x,y} \Pi_{ij}^{(xy)}(\vec{t}). \quad (2.105)$$

by equation (2.102) we can also write

$$S_{r12\dots ns}^c = \sum_{\{p\}} \Pi_{ij} \gamma_{ij}(R_{ij}), \quad (2.106)$$

where p is the set $r,1,2\dots n,s$.

If we add up all $S^c_{r12\dots ns}$ such that the p vertices in a cycle are allowed all distinguishable arrangements treating like defects as indistinguishable, the result is from equations (2.105) and (2.106)

$$B_v \int_{B.Z.} d\vec{t} \sum_{x,y} \Sigma^{11} \prod_{1j} w_{1j}^{(xy)}(\vec{t}) = c_v^{p_v} c_I^{p_I} \sum_{\{p\}} \Sigma^{11} \prod (-\lambda q_{1j} Z_1 Z_j), (2.107)$$

where Σ^{11} is defined as in equation (2.92). From equations (2.92) and (2.107) we have

$$S^c = \sum_{n \geq 2} \frac{B_v \Delta}{B(2\pi)^3} \int_{B.Z.} d\vec{t} \sum_{x,y} \Sigma^{11} \prod_{1j} w_{1j}^{(xy)}(t). \quad (2.108)$$

We shall now rewrite equation (2.108) via matrix notation. Let the allowed sites of defects i and j in the unit cell be the positions labeled a, b, c, \dots , and f, g, h, \dots , respectively. We define the matrix $\bar{w}_{1j}(t)$ by

$$\bar{w}_{1j}(t) = \begin{bmatrix} w_{1j}^{(af)} & w_{1j}^{(ag)} & w_{1j}^{(ah)} & \dots \\ w_{1j}^{(bf)} & w_{1j}^{(bg)} & & \\ w_{1j}^{(cf)} & \vdots & & \\ \vdots & \vdots & & \end{bmatrix} \quad (2.109)$$

For a crystal with interstitial and vacancy defects we define the matrix $\Omega(t)$ by

$$\Omega(t) = \begin{bmatrix} \bar{w}_{VV}(t) & \bar{w}_{VI}(t) \\ \bar{w}_{IV}(t) & \bar{w}_{II}(t) \end{bmatrix} \quad (2.110)$$

Since for our particular case the vacancy can take position 1 in the unit cell and the interstitial can take either position 2 or 3 in the unit cell, we have from equation (2.109)

$$\begin{aligned}\bar{w}_{VV}(t) &= w_{VV}^{(11)} & \bar{w}_{VI}(t) &= \begin{bmatrix} w_{VI}^{(12)} & w_{VI}^{(13)} \end{bmatrix} \\ \bar{w}_{IV}(t) &= \begin{bmatrix} w_{IV}^{(21)} \\ w_{IV}^{(31)} \end{bmatrix} & \bar{w}_{II}(t) &= \begin{bmatrix} w_{II}^{(22)} & w_{II}^{(23)} \\ w_{II}^{(32)} & w_{II}^{(33)} \end{bmatrix} \quad (2.111)\end{aligned}$$

so that

$$\Omega(t) = \begin{bmatrix} w_{VV}^{(11)} & w_{VI}^{(12)} & w_{VI}^{(13)} \\ w_{IV}^{(21)} & w_{II}^{(22)} & w_{II}^{(23)} \\ w_{IV}^{(31)} & w_{II}^{(32)} & w_{II}^{(33)} \end{bmatrix} \quad (2.112)$$

If we multiply together Ω^p matrices we call the result Ω^p . The trace of Ω^p gives a sum of products each composed of p w_{ij} functions. The terms correspond to all possible compositions such that $p_V + p_I = p$. To see how this works we will consider the case $p=2$. For $p=2$

$$\begin{aligned}\text{Tr} \Omega^2 &= w_{VV}^{(11)^2} + w_{VI}^{(12)} w_{IV}^{(21)} + w_{VI}^{(13)} w_{IV}^{(31)} + w_{IV}^{(21)} w_{VI}^{(12)} + w_{II}^{(22)^2} \\ &\quad + w_{II}^{(23)} w_{II}^{(32)} + w_{IV}^{(31)} w_{VI}^{(13)} + w_{II}^{(32)} w_{II}^{(23)} + w_{II}^{(33)^2} \quad (2.113)\end{aligned}$$

Equation (2.114) is a sum of products each composed of two w_{ij} , functions each term of which corresponds to a possible composition such that $p = 2$.

For each composition the terms appearing correspond to the defects being arranged on a cycle of distinguishable sites with like defects indistinguishable. Thus we have

$$S^c = \sum_{p \geq 2} \frac{B_V \Delta}{B^*(2\pi)^3} \int_{B.Z.} d\vec{t} \frac{\text{Tr} \Omega^p}{2^p}, \quad (2.114)$$

where the 2 appears because for every pattern generated from Ω^p the mirror image is also generated and the p appears because there are p possible choices for a first site in labeling the sites. Let $\theta_1, \theta_2, \dots, \theta_a$ be the eigenvalues of Ω so that

$$S^c = \sum_{p \geq 2} \frac{B_V \Delta}{(2\pi)^3 B^*} \int_{B.Z.} d\vec{t} \sum_{i=1}^a \frac{\theta_i^p}{2^p}. \quad (2.115)$$

From equations (2.81), (2.82), and (2.115) we see that the contributions of the cycle diagrams to $-\log \chi_V$ and $-\log \chi_I$ are respectively

$$T_{1V} = - \frac{B^*}{B_V} \frac{\partial S^c}{\partial c_V} = -\frac{1}{2} \frac{B_V \Delta}{B_V (2\pi)^3} \int_{B.Z.} d\vec{t} \left[\sum_{i=1}^a \frac{\theta_i}{1-\theta_i} \frac{\partial \theta_i}{\partial c_V} \right] \quad (2.116)$$

and

$$T_{1I} = - \frac{B^*}{B_I} \frac{\partial S^c}{\partial c_I} = -\frac{1}{2} \frac{B_V \Delta}{B_I (2\pi)^3} \int_{B.Z.} d\vec{t} \left[\sum_{i=1}^a \frac{\theta_i}{1-\theta_i} \frac{\partial \theta_i}{\partial c_I} \right]. \quad (2.117)$$

Note that we have used

$$\sum_{p \geq 2} \theta_i^{p-1} = \sum_{p \geq 1} \theta_i^p = \frac{\theta_i}{1-\theta_i}, \quad (2.118)$$

which is valid because θ_i is of order $w_{ij}^{(xy)}(t)$ which is less than one. To get an explicit expression for the cycle diagram contributions we need some information about the eigenvalues of Ω . However, we do not really need to find the eigenvalues. If we look back at equations (2.116) and (2.117) what we really need is

$$\sum_{i=1}^3 \frac{\theta_i}{1-\theta_i} \cdot \theta_i' = \sum_{i=1}^3 \frac{\theta_i}{1-\theta_i} \theta_i', \quad (2.119)$$

where the prime means partial differentiation either with respect to c_v or c_I .

We shall now show how we can get an expression for equation (2.119) in terms of the $w_{ij}^{(xy)}$. First we write out equation (2.119) and rearrange the result in a useful form to get

$$\begin{aligned} \sum_{i=1}^3 \frac{\theta_i}{1-\theta_i} \theta_i' &= \frac{\theta_1(1-\theta_2)(1-\theta_3)\theta_1' + \theta_2(1-\theta_3)(1-\theta_1)\theta_2' + \theta_3(1-\theta_1)(1-\theta_2)\theta_3'}{(1-\theta_1)(1-\theta_2)(1-\theta_3)} \\ &= [\theta_1\theta_1'^{1+\theta_2+\theta_3} + \theta_2\theta_2'^{1+\theta_1+\theta_3} + \theta_3\theta_3'^{1+\theta_1+\theta_2}] \\ &\quad - [\theta_1\theta_2\theta_3(\theta_1'^{1+\theta_2+\theta_3} + \theta_2'^{1+\theta_1+\theta_3} + \theta_3'^{1+\theta_1+\theta_2})] \\ &\quad - [\theta_1\theta_2(\theta_1'^{1+\theta_2} + \theta_2'^{1+\theta_1}) + \theta_2\theta_3(\theta_2'^{1+\theta_1+\theta_3} + \theta_3'^{1+\theta_1+\theta_2}) + \theta_3\theta_1(\theta_3'^{1+\theta_2+\theta_1} + \theta_1'^{1+\theta_2+\theta_3})] \\ &\quad \div \{1 - (\theta_1 + \theta_2 + \theta_3) - (\theta_1\theta_2\theta_3) + (\theta_1\theta_2 + \theta_2\theta_3 + \theta_3\theta_1)\} \quad (2.120) \end{aligned}$$

The form of the right hand side of equation (2.120) suggests that it might be written in terms of the traces of Ω ,

Ω^2 , and Ω^3 . We define

$$R_1 = \text{Tr} \Omega = \theta_1 + \theta_2 + \theta_3$$

$$R_2 = \text{Tr} \Omega^2 = \theta_1^2 + \theta_2^2 + \theta_3^2$$

$$R_3 = \text{Tr} \Omega^3 = \theta_1^3 + \theta_2^3 + \theta_3^3$$

$$R_4 = \frac{1}{2} (R_1^2 - R_2) = \theta_1 \theta_2 + \theta_2 \theta_3 + \theta_3 \theta_1$$

$$R_5 = R_1 R_2 - R_3 = \theta_1 \theta_2 (\theta_1 + \theta_2) + \theta_2 \theta_3 (\theta_2 + \theta_3) + \theta_3 \theta_1 (\theta_3 + \theta_1)$$

$$R_6 = \frac{1}{3} (R_1 R_4 - R_5) = \theta_1 \theta_2 \theta_3. \quad (2.121)$$

From equations (2.120) and (2.121) we have

$$\sum_{i=1}^3 \frac{\theta_i}{1-\theta_i} \theta_i^1 = \frac{\frac{1}{2} R_2^1 - R_6^1 R_1^1 - \frac{1}{3} (R_5^1 - R_2^1 R_1^1 + \frac{1}{3} R_3^1)}{1 - R_1 - R_6 + R_4}, \quad (2.122)$$

where the primes mean, as before, partial differentiation with respect to c_v or c_I .

Instead of now evaluating the R_i in terms of the w_{ij} we shall convert to a more streamlined notation. We define

$l_{ij}^{(xy)}$ by

$$w_{ij}^{(xy)} = -\lambda c_i Z_i Z_j l_{ij}^{(xy)}, \quad (2.123)$$

so that by equation (2.106) we have

$$l_{ij}^{(xy)} = \sum_{m \neq 1} e^{-i\vec{t} \cdot (\vec{R}_{1m} + \vec{\lambda}_{ij}^{(xy)})} q_{ij}(\vec{R}_{1m} + \vec{\lambda}_{ij}^{(xy)}). \quad (2.124)$$

We see at once from the crystal symmetry that

$$\begin{aligned} l_{VV}^{(11)} &= l_{II}^{(22)} = l_{II}^{(33)} \\ l_{VI}^{(12)} &= l_{IV}^{(21)} = l_{VI}^{(13)} = l_{IV}^{(31)} \\ l_{II}^{(23)} &= l_{II}^{(32)} \end{aligned} \quad (2.125)$$

which we abbreviate by

$$\begin{aligned} l_{VV}^{(11)} &= l_1 \\ l_{VI}^{(12)} &= l_{12} \\ l_{II}^{(23)} &= l_{23} \end{aligned} \quad (2.126)$$

Thus we have

$$\begin{aligned} w_{VV}^{(11)} &= -c_V \lambda l_1 \\ w_{VI}^{(12)} &= w_{IV}^{(13)} = c_V \lambda l_{12} \\ w_{IV}^{(21)} &= w_{IV}^{(31)} = c_I \lambda l_{12} \\ w_{II}^{(22)} &= w_{II}^{(33)} = -c_I \lambda l_1 \\ w_{II}^{(23)} &= -c_I \lambda l_{23} = w_{II}^{(32)} \end{aligned} \quad (2.127)$$

Substitution of equations (2.127) into equation (2.112) yields

$$\Omega = \lambda \begin{bmatrix} -c_V l_1 & c_V l_{12} & c_V l_{13} \\ c_I l_{12} & -c_I l_1 & -c_I l_{23} \\ c_I l_{13} & -c_I l_{23} & -c_I l_1 \end{bmatrix} \quad (2.128)$$

and hence

$$\begin{aligned} \text{Tr} \Omega &= -\lambda l_1 (c_V + 2c_I) \\ \text{Tr} \Omega^2 &= \lambda^2 [c_V^2 l_1^2 + 4c_V c_I l_{12}^2 + 2c_I^2 (l_1^2 + l_{23}^2)] \\ \text{Tr} \Omega^3 &= -\lambda^3 [c_V^3 l_1^3 + 6c_V^2 c_I l_1 l_{12}^2 + 2c_I^3 (l_1^3 + 3l_1 l_{23}^2) + 6c_V c_I^2 l_{12}^2 (l_1 + l_{23})]. \end{aligned} \quad (2.129)$$

From equations (2.121) and (2.129) we get

$$\begin{aligned} R_1 &= -\lambda l_1 (c_V + 2c_I) \\ R_2 &= \lambda^2 [c_V^2 l_1^2 + 4c_V c_I l_{12}^2 + 2c_I^2 (l_1^2 + l_{23}^2)] \\ R_3 &= -\lambda^3 [c_V^3 l_1^3 + 6c_V^2 c_I l_1 (l_{12}^2) + 2c_I^3 l_1 (l_1^2 + 3l_{23}^2) \\ &\quad + 6c_V c_I^2 l_{12}^2 (l_1 + l_{23})] \\ R_4 &= \lambda^2 [2c_V c_I (l_1^2 - l_{12}^2) + c_I^2 (l_1^2 - l_{23}^2)] \\ R_5 &= \lambda^3 [2c_V^2 c_I l_1 (l_{12}^2 - l_1^2) + 2c_I^3 l_1 (l_{23}^2 - l_1^3) - 2c_V c_I^2 l_1 \\ &\quad \cdot (l_{12}^2 + l_1^2 + l_{23}^2) + 6c_V c_I^2 l_{12}^2 l_{23}] \\ R_6 &= \lambda^3 c_V c_I^2 [l_1 (2l_{12}^2 + l_{23}^2 - l_1^2) - 2l_{12}^2 l_{23}]. \end{aligned} \quad (2.130)$$

We also need the derivatives of R_1, R_2, R_3 , and R_5 . They are

$$\frac{\partial R_1}{\partial c_v} = -\lambda l_1 \quad \frac{\partial R_2}{\partial c_v} = 2 \lambda^2 c_v l_1^2 + 4 \lambda^2 c_I l_{12}^2$$

$$\frac{\partial R_3}{\partial c_v} = -3\lambda^3 c_v^2 l_1^3 - 12 \lambda^3 c_v c_I l_1 l_{12}^2 - 6 \lambda^3 c_I^2 l_{12}^2 (l_1 + l_{23}) \quad (2.131)$$

$$\frac{\partial R_5}{\partial c_v} = 4\lambda^3 c_v c_I l_1 (l_{12}^2 - l_1^2) - 2\lambda^3 c_I^2 [l_1 (l_{12}^2 + l_1^2 + l_{23}^2) - 3l_{12}^2 l_{23}] .$$

and

$$\frac{\partial R_1}{\partial c_I} = -2\lambda l_1 \quad \frac{\partial R_2}{\partial c_I} = 4\lambda^2 c_v l_{12}^2 + 4\lambda^2 c_I (l_1^2 + l_{23}^2)$$

$$\frac{\partial R_3}{\partial c_I} = -6\lambda^3 [c_v^2 l_1 l_{12}^2 + c_I^2 l_1 (l_1^2 + 3l_{23}^2) + 2c_v c_I l_{12}^2 (l_1 + l_{23})]$$

(2.132)

$$\frac{\partial R_5}{\partial c_I} = 2\lambda^3 c_v^2 l_1 (l_{12}^2 - l_1^2) + 6\lambda^3 c_I^2 l_1 (l_{23}^2 - l_1^2) - 4\lambda^3 c_v c_I$$

$$[l_1 (l_{12}^2 + l_1^2 + l_{23}^2) - 3l_{12}^2 l_{23}] .$$

From equations (2.131), (2.130), and (2.122) we obtain

$$\sum_{i=1}^3 \frac{\theta_i}{1-\theta_i} \frac{\theta_i}{c_v} = \lambda^2 [c_v l_1^2 + 2c_I l_{12}^2]$$

$$+ \lambda^4 c_v c_I^2 l_1 [l_1 (2l_{12}^2 + l_{23}^2 - l_1^2) - 2l_{12}^2 l_{23}]$$

$$+ 2\lambda^3 c_I^2 l_{12}^2 (l_1 - l_{23}) - 2\lambda^3 c_v c_I l_1 (l_{12}^2 - l_1^2)$$

$$\div \{1 + \lambda l_1(c_v + 2c_I) + \lambda^2[2c_v c_I(l_1^2 - l_{12}^2) + c_I^2(l_1^2 - l_{23}^2)] \\ - \lambda^3 c_v c_I^2 [l_1(2l_{12}^2 + l_{23}^2 - l_1^2) - 2l_{12}^2 l_{23}] \}. \quad (2.133)$$

Similarly, from equations (2.132), (2.130), and (2.122) we obtain

$$\sum_{i=1}^3 \frac{\theta_i}{1-\theta_i} \frac{1}{c_I} = 2\lambda^2 [c_v l_{12}^2 + c_I(l_1^2 + l_{23}^2)] \\ + 2\lambda^4 c_v c_I^2 l_1 [l_1(2l_{12}^2 + l_{23}^2 - l_1^2) - 2l_{12}^2 l_{23}] \\ + 2\lambda^3 c_I^2 l_1(l_1^2 - l_{23}^2) + 2\lambda^3 c_v c_I [l_1(l_1^2 + l_{23}^2) - 2l_{12}^2 l_{23}] \quad (2.134) \\ \div \{1 + \lambda l_1(c_v + 2c_I) + \lambda^2[2c_v c_I(l_1^2 - l_{12}^2) + c_I^2(l_1^2 - l_{23}^2)] \\ - \lambda^3 c_v c_I^2 [l_1(2l_{12}^2 + l_{23}^2 - l_1^2) - 2l_{12}^2 l_{23}] \}.$$


We shall later substitute these expressions into equations (2.116) and (2.117).

3. Contributions of S^R and S^e to the activity coefficients

Let us consider the contribution of S^R to $-\log \chi_v$ and $-\log \chi_I$. We shall again make use of the ideas concerning prototype patterns introduced after equation (2.87). S^R may be written as the sum of contributions from the different prototype patterns and the patterns derived from these by replacing q bonds by q bond chains as discussed earlier. This is written

$$S^R = \sum_{\sigma(m)} S[\sigma(m)], \quad (2.135)$$

where $S[\sigma(m)]$ is the sum of all contributions of the prototype pattern $\sigma(m)$ and all patterns derived from it.

Diagrams of the form  must be excluded since they belong to S^e and the diagrams



are excluded because they belong to S^c . Recall that $p=m+n$ (2.136) where p is the number of vertices in the pattern $\tau(p)$, m is the number of vertices in the prototype pattern $\sigma(m)$, and n is the number of vertices involved in q bond chains. We also define

$$p_V = m_V + n_V$$

$$p_I = m_I + n_I$$

$$m = m_V + m_I$$

$$n = n_V + n_I \quad . \quad (2.137)$$

Thus from equations (2.88) and (2.89) we obtain

$$S[\sigma(m)] = \sum_{n \geq 0} \frac{c_V^{m_V+n_V}}{(m_V+n_V)!} \frac{c_I^{m_I+n_I}}{(m_I+n_I)!} \left\{ \sum_{\{m+n\}} \frac{M[\sigma(m)]}{B^*} \cdot \frac{(m_V+n_V)! (m_I+n_I)!}{m_V! m_I! \prod_{l=1}^q n_{lV}! n_{lI}!} \right. \\ \left. \times \sum_{h(n)} R[\sigma(m); h(n), \dots, h(n)] \right\} . \quad (2.138)$$

The last summation is over all possible arrangements of vertices in each of the q bond chains. $M[\sigma(m)]$ is the number of times the prototype pattern $\sigma(m)$ appears in S^R .

The factor

$$\frac{(m_V+n_V)!(m_I+n_I)!}{m_V!m_I! \prod_{l=1}^q n_{lV}!n_{lI}!} \quad (2.139)$$

is the number of ways of choosing the sets m and n_1, n_2, \dots, n from the set $m+n$. In q bond chain l like defects may be interchanged in $n_{lV}!n_{lI}!$ ways so equation (2.138) becomes


$$S[\sigma(m)] = \sum_{n \geq 0} \frac{c_V^{m_V+n_V}}{m_V!} \frac{c_I^{m_I+n_I}}{m_I!} \sum_{\{m+n\}} \frac{M[\sigma(m)]}{B^*} \Sigma^{ll} R[\sigma(m); h(n_1), \dots, h(n_q)], \quad (2.140)$$

where the double prime on the summation means that only defects corresponding to different defect types are to be indistinguishable. We now rearrange equation (2.140) obtaining


$$S[\sigma(m)] = \frac{c_V^{m_V}}{m_V!} \frac{c_I^{m_I}}{m_I!} \sum_{\{m\}} M[\sigma(m)] \sum_{n \geq 0} \frac{c_V^{n_V} c_I^{n_I}}{B^*} \Sigma^{ll} R[\sigma(m); h(n_1), \dots, h(n_q)], \quad (2.141)$$

For a particular prototype pattern $\sigma(m)$ let defects i and j belong to the set m and let there be ν_{ij} direct q bonds and q bond chains between i and j . Then we have

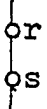
$$\sum_{n \geq 0} \sum_{\{n\}} \Sigma^{ll} R[\sigma(m); h(n_1), \dots, h(n_q)] c_V^{n_V} c_I^{n_I} = \delta[\sigma(m)] \prod_{i,j \in m} \frac{(-\lambda Z_i Z_j)^{\nu_{ij}}}{\nu_{ij}!} \sum_{l=1}^q \sum_{n_l \geq 0} L(n_l, R_{ij}), \quad (2.142)$$

where $\delta[\sigma(m)]$ is the product of δ bonds in $\sigma(m)$. $\prod_{i,j \in m}$ denotes a product of terms, one for every pair of directly connected vertices in $\sigma(m)$, and $L(n_l; R_{ij})$ is the sum over all configurations of the sum of products of q bonds corresponding to every arrangement of the n_l vertices, like vertices being indistinguishable. To make this more transparent we consider some particular cases. Consider the prototype diagram . This will have $\nu_{ij}=3$. The product corresponding to the prototype diagram has $n_l=0$ for $l=1,2,3$, so that

$$\prod_{l=1}^3 L(n_l; R_{ij}) = [L(0; R_{ij})]^3 = q_{ij}^3. \quad (2.143)$$

If we replace a single direct q bond by the chain  we have

$$\begin{aligned} \prod_{l=1}^3 L(n_l; R_{ij}) &= L(1; R_{ij}) L(0; R_{ij}) L(0; R_{ij}) \\ &= q_{is} q_{sj} (-\lambda Z_s^2) q_{ij}^2. \end{aligned} \quad (2.144)$$

If we begin replacing single direct q bonds by chains with more than one vertex we must remember that different defect types are distinguishable. For example, replacing one of the q bonds by  where r and s are different type defects yields

$$\prod_{l=1}^3 L(n_l; R_{ij}) = L(2; R_{ij}) L(0; R_{ij}) L(0; R_{ij}) \quad (2.145)$$

with

$$L(2; R_{1j}) = q_{ir} q_{rs} q_{sj} (\lambda^2 Z_r^2 Z_s^2) + q_{is} q_{sr} q_{rj} (\lambda^2 Z_s^2 Z_r^2). \quad (2.146)$$

We now note that removal of a bond from a cycle diagram converts the diagram from a cycle to a chain. Recall that the trace of Ω gives all distinguishable arrangements of defects in a cycle of labeled positions treating like defects as indistinguishable. From equations (2.107), (2.108) and (2.114) we have

$$\sum_{n_1 \geq 0} L(n_1, R_{1j}) = \frac{\Delta}{(2\pi)^3} \int d\vec{t} \frac{e^{i\vec{t} \cdot \vec{R}_{1j}}}{c_j} \frac{\partial}{\partial w_{1j}^{(xy)}} \left[\sum_{s \geq 2} \frac{\text{Tr}(\Omega^s)}{s} \right]. \quad (2.147)$$

The differentiation removes a bond from each cycle leaving a chain between 1 and j. The s occurs in the denominator because there are s possible choices for a first site in labeling positions. The c_j appears in the denominator because $\partial/\partial w_{1j}^{(xy)}$ removes c_1 but not c_j and we only want $c_v^{n_v} c_I^{n_I}$ to appear (see equation (2.142)).

Now, again using the eigenvalues of Ω we obtain

$$\begin{aligned} \sum_{n \geq 2} \frac{\partial}{\partial w_{1j}^{(xy)}} \left[\frac{\text{Tr}(\Omega^n)}{n} \right] &= \frac{\partial}{\partial w_{1j}^{(xy)}} \left[\sum_{i=1}^a [-\log(1-\theta_i) - \theta_i] \right] \\ &= \sum_{i=1}^a \frac{\theta_i}{1-\theta_i} \theta_i^1, \end{aligned} \quad (2.148)$$

which we shall evaluate much like we did equation (2.119), except that the prime on θ_i now denotes differentiation with respect to $w_{1j}^{(xy)}$. In fact, by changing the meaning

of the primes equation (2.122) still holds. We now need the R_i in terms of the $w_{ij}^{(xy)}$. These are (see equations (2.121)):

$$R_1 = w_{VV}^{(11)} + w_{II}^{(22)} + w_{II}^{(33)}$$

$$R_2 = w_{VV}^{(11)^2} + w_{II}^{(22)^2} + w_{II}^{(33)^2} + 2[w_{VI}^{(12)} w_{IV}^{(21)} + w_{VI}^{(13)} w_{IV}^{(31)} + w_{II}^{(23)} w_{II}^{(32)}]$$

$$R_3 = w_{VV}^{(11)^3} + w_{II}^{(22)^3} + w_{II}^{(33)^3} + 3[w_{IV}^{(12)} w_{VI}^{(21)} (w_{VV}^{(11)} + w_{II}^{(22)}) + w_{IV}^{(13)} w_{VI}^{(31)} (w_{VV}^{(11)} + w_{II}^{(33)}) + w_{II}^{(23)} w_{II}^{(32)} (w_{II}^{(22)} + w_{II}^{(33)}) + w_{VI}^{(12)} w_{II}^{(23)} w_{IV}^{(31)} + w_{VI}^{(13)} w_{II}^{(32)} w_{IV}^{(21)}]$$

$$R_4 = w_{VV}^{(11)} w_{II}^{(22)} + w_{VV}^{(11)} w_{II}^{(33)} + w_{II}^{(22)} w_{II}^{(33)} - w_{VI}^{(12)} w_{IV}^{(21)} - w_{VI}^{(13)} w_{IV}^{(31)} - w_{II}^{(23)} w_{II}^{(32)}$$

$$R_5 = w_{VV}^{(11)^2} (w_{II}^{(22)} + w_{II}^{(33)}) + w_{II}^{(22)^2} (w_{II}^{(33)} + w_{VV}^{(11)}) + w_{II}^{(33)^2} \cdot (w_{VV}^{(11)} + w_{II}^{(22)})$$

$$- 3(w_{VI}^{(12)} w_{II}^{(23)} w_{IV}^{(31)} + w_{VI}^{(13)} w_{II}^{(32)} w_{IV}^{(21)}) + w_{VI}^{(13)} w_{IV}^{(31)} \cdot (2w_{II}^{(22)} - w_{VV}^{(11)} - w_{II}^{(33)})$$

$$+ w_{VI}^{(12)} w_{IV}^{(21)} (2w_{II}^{(33)} - w_{VV}^{(11)} - w_{II}^{(22)}) + w_{II}^{(23)} w_{II}^{(32)} \cdot (2w_{VV}^{(11)} - w_{II}^{(22)} - w_{II}^{(33)})$$

$$R_6 = w_{VV}^{(11)} w_{II}^{(22)} w_{II}^{(33)} + w_{VI}^{(12)} w_{II}^{(23)} w_{IV}^{(31)} + w_{VI}^{(13)} w_{II}^{(32)} w_{IV}^{(21)} \\ - w_{VI}^{(13)} w_{IV}^{(31)} w_{II}^{(22)} - w_{VI}^{(12)} w_{IV}^{(21)} w_{II}^{(33)} - w_{II}^{(23)} w_{II}^{(32)} w_{VV}^{(11)}.$$

(2.149)

We also need the derivatives of R_1, R_2, R_3 , and R_5 with respect to the nine different $w_{ij}^{(xy)}$. These are

$$\frac{\partial R_1}{\partial w_{VV}^{(11)}} = \frac{\partial R_1}{\partial w_{II}^{(22)}} = \frac{\partial R_1}{\partial w_{II}^{(33)}} = 1$$

$$\frac{\partial R_1}{\partial w_{VI}^{(12)}} = \frac{\partial R_1}{\partial w_{IV}^{(21)}} = \frac{\partial R_1}{\partial w_{VI}^{(13)}} = \frac{\partial R_1}{\partial w_{IV}^{(31)}} = \frac{\partial R_1}{\partial w_{II}^{(23)}} = \frac{\partial R_1}{\partial w_{II}^{(32)}} = 0$$

$$\frac{\partial R_2}{\partial w_{VV}^{(11)}} = 2w_{VV}^{(11)} \quad \frac{\partial R_2}{\partial w_{II}^{(22)}} = 2w_{II}^{(22)} \quad \frac{\partial R_2}{\partial w_{II}^{(33)}} = 2w_{II}^{(33)}$$

$$\frac{\partial R_2}{\partial w_{VI}^{(12)}} = 2w_{IV}^{(21)} \quad \frac{\partial R_2}{\partial w_{VI}^{(13)}} = 2w_{IV}^{(31)} \quad \frac{\partial R_2}{\partial w_{II}^{(23)}} = 2w_{II}^{(32)}$$

$$\frac{\partial R_2}{\partial w_{IV}^{(21)}} = 2w_{VI}^{(12)} \quad \frac{\partial R_2}{\partial w_{IV}^{(31)}} = 2w_{VI}^{(13)} \quad \frac{\partial R_2}{\partial w_{II}^{(32)}} = 2w_{II}^{(23)}$$

$$\frac{\partial R_3}{\partial w_{VV}^{(11)}} = 3(w_{VV}^{(11)})^2 + w_{VI}^{(13)} w_{IV}^{(31)} + w_{VI}^{(12)} w_{IV}^{(21)},$$

$$\frac{\partial R_3}{\partial w_{II}^{(22)}} = 3(w_{II}^{(22)})^2 + w_{VI}^{(12)} w_{IV}^{(21)} + w_{II}^{(23)} w_{II}^{(32)},$$

$$\frac{\partial}{\partial R_3} \frac{\partial}{\partial w} \frac{I}{V} (12) = 3(w(23)w(31) + w(21)w(11)w(11) + w(22)w(22))$$

$$\frac{\partial}{\partial R_3} \frac{\partial}{\partial w} \frac{I}{V} (21) = 3(w(13)w(32) + w(12)w(11)w(11) + w(22)w(22))$$

$$\frac{\partial}{\partial R_3} \frac{\partial}{\partial w} \frac{I}{V} (13) = 3(w(32)w(21) + w(31)w(11)w(11) + w(33)w(33))$$

$$\frac{\partial}{\partial R_3} \frac{\partial}{\partial w} \frac{I}{V} (31) = 3(w(12)w(23) + w(13)w(11)w(11) + w(33)w(33))$$

$$\frac{\partial}{\partial R_3} \frac{\partial}{\partial w} \frac{I}{V} (23) = 3(w(12)w(31) + w(32)w(22) + w(33)w(33))$$

$$\frac{\partial}{\partial R_3} \frac{\partial}{\partial w} \frac{I}{V} (32) = 3(w(13)w(21) + w(23)w(22) + w(33)w(33))$$

$$\frac{\partial}{\partial R_5} \frac{\partial}{\partial w} \frac{I}{V} (11) = 2w(11)w(11) + w(22)w(22) + w(33)w(33)$$

$$+ 2w(23)w(32) - w(12)w(21) - w(13)w(31) - w(23)w(32) - w(23)w(32)$$

$$\frac{\partial}{\partial R_5} \frac{\partial}{\partial w} \frac{I}{V} (22) = 2w(22)w(11) + w(33)w(33) + w(11)w(11) + w(33)w(33)$$

$$+ 2w(13)w(31) - w(12)w(21) - w(13)w(31) - w(23)w(32) - w(23)w(32)$$

$$\frac{\partial R_5}{\partial w_{II}^{(33)}} = 2w_{II}^{(33)}(w_{VV}^{(11)} + w_{II}^{(22)}) + w_{VV}^{(11)^2} + w_{II}^{(22)^2}$$

$$+ 2w_{VI}^{(12)}w_{IV}^{(21)} - w_{VI}^{(13)}w_{IV}^{(31)} - w_{II}^{(23)}w_{II}^{(32)}$$

$$\frac{\partial R_5}{\partial w_{VI}^{(12)}} = -3w_{II}^{(23)}w_{IV}^{(31)} + w_{IV}^{(21)}(2w_{II}^{(33)} - w_{VV}^{(11)} - w_{II}^{(22)}),$$

$$\frac{\partial R_5}{\partial w_{IV}^{(21)}} = -3w_{VI}^{(13)}w_{II}^{(32)} + w_{VI}^{(12)}(2w_{II}^{(33)} - w_{VV}^{(11)} - w_{II}^{(22)}),$$

$$\frac{\partial R_5}{\partial w_{VI}^{(13)}} = -3w_{II}^{(32)}w_{IV}^{(21)} + w_{IV}^{(31)}(2w_{II}^{(22)} - w_{VV}^{(11)} - w_{II}^{(33)}),$$

$$\frac{\partial R_5}{\partial w_{IV}^{(31)}} = -3w_{VI}^{(12)}w_{II}^{(23)} + w_{VI}^{(13)}(2w_{II}^{(22)} - w_{VV}^{(11)} - w_{II}^{(33)}),$$

$$\frac{\partial R_5}{\partial w_{II}^{(23)}} = -3w_{VI}^{(12)}w_{IV}^{(31)} + w_{II}^{(32)}(2w_{VV}^{(11)} - w_{II}^{(22)} - w_{II}^{(33)}),$$

$$\frac{\partial R_5}{\partial w_{II}^{(32)}} = -3w_{VI}^{(13)}w_{IV}^{(21)} + w_{II}^{(23)}(2w_{VV}^{(11)} - w_{II}^{(22)} - w_{II}^{(33)}). \quad (2.150)$$

We now define a new quantity, R_7 , by

$$R_7 = 1 - R_1 - R_6 + R_4 \quad (2.151)$$

Combining equations (2.149) and (2.150) yields

$$R_7 = 1 - w_{VV}^{(11)} - w_{II}^{(22)} - w_{II}^{(33)} + w_{VV}^{(11)}(w_{II}^{(22)} + w_{II}^{(33)}),$$

$$\begin{aligned}
& + {}^w (22) (33) {}^{II} - {}^w (12) (21) {}^{IV} - {}^w (13) (31) {}^{IV} - {}^w (23) (32) {}^{II} \\
& - {}^w (11) (22) (33) {}^{II} - {}^w (12) (23) (31) {}^{IV} - {}^w (13) (32) (21) {}^{IV} \\
& + {}^w (13) (31) (22) {}^{II} + {}^w (12) (21) (33) {}^{IV} + {}^w (23) (32) (11) {}^{VV} .
\end{aligned}$$

(2.152)

From equations (2.148), (2.149), (2.150), (2.152), and

(2.123) we obtain

$$\frac{1}{3} \frac{\partial}{\partial \theta_k} \frac{\partial}{\partial \theta_k} {}^w (11) {}^{VV} = \{ -\lambda_1 I_1 + \lambda_2 c_I (1_2^{12} + 1_2^{13} - 21_2^1) \}$$

$$-\lambda_3 c_I^2 [1_1 (1_2^{13} + 1_2^{12} - 21_2^1) - 21_3^{13} 1_2^{12}] / R_7$$

$$\frac{1}{3} \frac{\partial}{\partial \theta_k} \frac{\partial}{\partial \theta_k} {}^w (22) {}^{II} = \{ -\lambda_1 I_1 + \lambda_2 [c_V (1_2^{12} - 1_2^1) + c_I (1_2^{23} - 1_2^1)] \}$$

$$-\lambda_3 c_V c_I [1_1 (1_2^{13} + 1_2^{12} - 21_2^1) - 21_3^{13} 1_2^{12}] / R_7$$

$$\frac{1}{3} \frac{\partial}{\partial \theta_k} \frac{\partial}{\partial \theta_k} {}^w (33) {}^{II} = \{ -\lambda_1 I_1 + \lambda_2 [c_V (1_2^{13} - 1_2^1) + c_I (1_2^{23} - 1_2^1)] \}$$

$$-\lambda_3 c_V c_I [1_1 (1_2^{13} + 1_2^{12} - 21_2^1) - 21_3^{13} 1_2^{12}] / R_7$$

$$\frac{1}{3} \frac{\partial}{\partial \theta_k} \frac{\partial}{\partial \theta_k} {}^w (12) {}^{VI} = \frac{R_7}{\lambda_1 1_2 + \lambda_2 c_I (1_1 1_2 - 1_3 1_2)}$$

$$= \frac{1}{c_V} \sum_{k=1}^3 \frac{\theta_k}{1-\theta_k} \frac{\partial \theta_k}{\partial w_{IV}^{(21)}}$$

$$\frac{1}{c_I} \sum_{k=1}^3 \frac{\theta_k}{1-\theta_k} \frac{\partial \theta_k}{\partial w_{VI}^{(13)}} = \frac{\lambda l_{13} + \lambda^2 c_I (l_{11} l_{13} - l_{12} l_{23})}{R_7}$$

$$= \frac{1}{c_V} \sum_{k=1}^3 \frac{\theta_k}{1-\theta_k} \frac{\partial \theta_k}{\partial w_{IV}^{(31)}}$$

$$\frac{1}{c_I} \sum_{k=1}^3 \frac{\theta_k}{1-\theta_k} \frac{\partial \theta_k}{\partial w_{II}^{(23)}} = - \frac{\lambda l_{23} + \lambda^2 c_V (l_{11} l_{23} - l_{12} l_{13})}{R_7}$$

$$= \frac{1}{c_I} \sum_{k=1}^3 \frac{\theta_k}{1-\theta_k} \frac{\partial \theta_k}{\partial w_{II}^{(32)}} , \quad (2.153)$$

and

$$R_7 = 1 + \lambda l_1 (c_V + 2c_I) + \lambda^2 [c_V c_I (2l_1^2 - l_{12}^2 - l_{13}^2) + c_I^2 (l_1^2 - l_{23}^2)] - \lambda^3 c_V c_I^2 [l_1 (l_{13}^2 + l_{12}^2 + l_{23}^2 - l_1^2) - 2l_{13} l_{23} l_{12}]. \quad (2.154)$$

We now define the functions, m_{ij} , by

$$m_{ij} = - \lambda Z_i Z_j \sum_{n_1 \geq 0} L(n_1; R_{ij}), \quad (2.155)$$

so that

$$S^R = \sum_{m \geq 2} \frac{c_V^{m_V} c_I^{m_I}}{m_V! m_I!} \sum_{\sigma(m)} \sum_{\{m\}} \frac{M[\sigma(m)]}{B} \prod_{i,j \in m} \frac{m_{ij}}{z_{ij}^{z'_{ij}}} \quad (2.156)$$

follows from equations (2.135), (2.141), (2.142), (2.147), and (2.155).

From equations (2.155) and (2.147) we have that

$$m_{ij} = -\lambda Z_i Z_j \frac{\Delta}{(2\pi)^3} \int_{B.Z.} d\vec{t} \frac{e^{i\vec{t} \cdot \vec{R}_{ij}}}{c_j} \sum_{l=1}^3 \frac{\theta_l}{1-\theta_l} \frac{\partial \theta_l}{\partial w_{ij}^{(xy)}} \quad (2.157)$$

We shall later use equations (2.153) and (2.157) to get asymptotic expressions for the m_{ij} .

The equation for S^e defined by equation (2.90) is

$$S^e = -\frac{\lambda}{4\pi B^*} \sum_i \sum_j c_i c_j \sum_{\{ij\}} \frac{Z_i Z_j}{R_{ij}}. \quad (2.158)$$

We now have expressions for S^R , S^c , and S^e . In the next section we shall evaluate the Fourier transforms, l_1 , l_{12} , and l_{23} .

D. Fourier Transforms of the Coulomb Potentials

1. Asymptotic expressions

The integrand appearing in equation (2.157) for m_{ij} oscillates rapidly for large t so that if we extend the upper limit of integration from the Brillouin zone edge to infinity we expect negligible contribution from that region. The major contribution will come from the small t region, $t \ll 1/A$. Consequently we use the small t approximations for l_1 , l_{12} , and l_{23} and the range of integration for equation (2.157) becomes zero to infinity.

For an infinite lattice Born and Bradburn (1943) have shown that equation (2.124) can be split into a sum over the direct lattice and a sum over the reciprocal lattice. These sums can be adjusted to give the most rapid convergence of both sums. Their method is similar to the theta function transformation of Ewald (1921). The small t approximations can be easily obtained from their expressions. The resulting form is

$$\Delta l_{ij} = -A^2 b_{ij} + \frac{1}{t^2}, \quad (2.159)$$

where Δ is the volume of the unit cell for the crystal structure under consideration and A is the lattice parameter. The structure dependent parameters, b_{ij} , have been worked out for simple, face centered, and body centered cubic structures (Misra, 1940).

The Fourier transforms which we call l_1 and l_{23} (see equations (2.124) and (2.126)) are the same as for Schottky disorder. We then have from Allnatt and Cohen's paper

$$\Delta l_1 = -A^2 b_1 + \frac{1}{t^2}$$

$$\Delta l_{23} = -A^2 b_{23} + \frac{1}{t^2}$$

with

$$b_1 = 0.36485$$

$$b_{23} = 0.08673 \quad (2.160)$$

Since l_{12} is the transform of interactions between ions on the interstitial lattice and vacancies on the perfect lattice there is no corresponding transform in the theory of Schottky disorder.

From Fig. 1 we see that picking one of the interstitials as origin and obtaining the Fourier transform of the body centered structure includes l_{12} . In fact if we subtract out the Fourier transform corresponding to the simple cubic structure we have just $2l_{12}$. Thus, we have

$$\Delta l_{12} = \frac{1}{2}(l_{\text{BCC}} - l_{\text{SC}}), \quad (2.161)$$

where

$$\Delta_{\text{BCC}} l_{\text{BCC}} = -A_{\text{BCC}}^2 0.57920 + \frac{1}{t^2},$$

$$\Delta_{\text{SC}} l_{\text{SC}} = -A_{\text{SC}}^2 0.22579 + \frac{1}{t^2}. \quad (2.162)$$

The appropriate lattice parameters are

$$\begin{aligned} A_{\text{BCC}} &= \frac{A}{2} & \Delta_{\text{BCC}} &= 4A_{\text{BCC}}^3 \\ A_{\text{SC}} &= A & \Delta_{\text{SC}} &= A_{\text{SC}}^3. \end{aligned} \quad (2.163)$$

From equations (2.161), (2.162), and (2.163) we obtain

$$\Delta l_{12} = -A^2 b_{12} + \frac{1}{t^2}$$

with

$$b_{12} = 0.06381. \quad (2.164)$$

The continuum values for the Fourier transforms are given by

$$\begin{aligned}\Delta l_1 &= \frac{1}{t^2} \\ \Delta l_{12} &= \frac{1}{t^2} \\ \Delta l_{23} &= \frac{1}{t^2} .\end{aligned}\tag{2.165}$$

These correspond to allowing the real lattice spacing to approach zero. Alternatively we can replace the sum in equation (2.124) by an integral to get the same results.

2. Asymptotic forms for the m_{1j}

To obtain expressions for the m_{1j} we employ the small t expressions for the Fourier transforms and extend the integral over all of reciprocal space. Equation (2.157) therefore becomes

$$\begin{aligned}m_{1j} &= -\lambda Z_1 Z_j \frac{\Delta}{(2\pi)^3} \int_0^\infty \frac{(2\pi)^3}{\Delta} d\vec{t} e^{i\vec{t} \cdot \vec{R}_{1j}} \frac{E_{1j} + D_{1j} t^2}{F^{-1} t^2 + K^2 G} \\ &= -\lambda Z_1 Z_j \int_0^\infty d\vec{t} e^{i\vec{t} \cdot \vec{R}_{1j}} \left[\frac{F(E_{1j} - K^2 L^2 D_{1j})}{t^2 + K^2 L^2} + D_{1j} F \right] \\ &= \frac{\lambda Z_1 Z_j}{4\pi R_{1j}} F(E_{1j} - K^2 L^2 D_{1j}) e^{-KLR_{1j}} .\end{aligned}\tag{2.166}$$

where

$$F = \left\{ 1 - K^2 A^2 b_1 + \frac{K^4 A^4}{16} (5b_1^2 - 4b_3^2 - b_2^2) - \frac{K^6 A^6}{32} (b_1^3 + 2b_2 b_3^2 - b_1 b_2^2 - 2b_1 b_3^2) \right\}^{-1}$$

$$L^2 = FG = F \left\{ 1 + \frac{K^2 A^2}{8} (4b_3 - 5b_1 + b_2) - \frac{K^4 A^4}{32} (b_2^2 + 4b_1 b_3 + 2b_1 b_2 - 3b_1^2 - 4b_2 b_3) \right\}$$

$$E_{11} = -1 + K^2 A^2 (b_1 - b_3) - \frac{K^4 A^4}{16} (b_2^2 + 4b_1 b_3 + 2b_1 b_2 - 3b_1^2 - 4b_2 b_3)$$

$$E_{22} = E_{33} = -1 + \frac{K^2 A^2}{2} (3b_1 - 2b_3 - b_2) - \frac{K^4 A^4}{8} (b_2^2 + 4b_1 b_3 + 2b_1 b_2 - 3b_1^2 - 4b_2 b_3)$$

$$E_{12} = E_{21} = E_{13} = E_{31} = -1 + \frac{K^2 A^2}{4} (b_1 - b_2)$$

$$E_{23} = E_{32} = -1 - \frac{K^2 A^2}{2} (2b_3 - b_1 - b_2)$$

$$D_{11} = A^2 \left[b_1 + \frac{K^2 A^2}{2} (b_3^2 - b_1^2) - \frac{K^4 A^4}{16} (b_1^3 + 2b_2 b_3^2 - b_1 b_2^2 - 2b_1 b_3^2) \right]$$

$$D_{22} = D_{33} = A^2 \left[b_1 + \frac{K^2 A^2}{4} (b_2^2 + 2b_3^2 - 3b_1^2) - \frac{K^4 A^4}{8} (b_1^3 + 2b_2 b_3^2 - b_1 b_2^2 - 2b_1 b_3^2) \right]$$

$$D_{12} = D_{21} = D_{13} = D_{31} = A^2 \left[b_3 + \frac{K^2 A^2}{4} (b_2 - b_1) b_3 \right]$$

$$D_{23} = D_{32} = A^2 \left[b_2 + \frac{K^2 A^2}{2} (b_3^2 - b_1 b_2) \right]. \quad (2.167)$$

These expressions for m_{ij} will be used shortly to evaluate the first order contributions of S^R to the activity coefficients.

The quantity K , the inverse of the Debye-Hückel screening radius, is defined by

$$K^2 = \frac{4\lambda c_I}{\Delta}. \quad (2.168)$$

E. Contributions to the Activity Coefficients in Final Form

1. Contributions of the cycle diagrams

From equations (2.116) and (2.133) we have

$$\begin{aligned} T_{1V} = & -\frac{1}{2} \frac{\Delta}{(2\pi)^3} \int d\vec{t} \left\{ \lambda^2 (c_V l_1^2 + 2c_I l_{12}^2) \right. \\ & + \lambda^4 c_V c_I^2 l_1 [l_1 (2l_{12}^2 + l_{23}^2 - l_1^2) - 2 l_{12}^2 l_{23}] \\ & \left. - \lambda^3 [c_V c_I^2 l_1 (l_{12}^2 - l_1^2) + c_I^2 (l_1 - l_{23})^2 l_{12}^2] \right\} / R_7. \quad (2.169) \end{aligned}$$

Similarly from equations (2.117) and (2.134) it follows that

$$\begin{aligned} T_{1I} = & -\frac{1}{4} \frac{\Delta}{(2\pi)^3} \int d\vec{t} \left\{ 2\lambda^2 (c_V l_{12}^2 + c_I (l_1^2 + l_{23}^2)) \right. \\ & + 2 \lambda^4 c_V c_I^2 l_1 [l_1 (2 l_{12}^2 + l_{23}^2 - l_1^2) - 2 l_{12}^2 l_{23}] \\ & \left. + 2 \lambda^3 c_I [c_I l_1 (l_1^2 - l_{23}^2) + c_V (l_1 (l_1^2 - l_{23}^2) - 2 l_{12}^2 l_{23})] \right\} / R_7 \quad (2.170) \end{aligned}$$

The approximation we make here is to let the real lattice spacing approach zero by employing equations (2.165). In this limit we have

$$\begin{aligned}
T_{1V} &= -\frac{1}{2} \frac{\Delta}{(2\pi)^3} \int_0^\infty 4\pi t^2 dt \left[\frac{K^4}{4c_I} \frac{1}{t^4 + K^2 t^2} \right] \\
&= -\frac{1}{2} \left(\frac{e^2}{DKT} \right) K,
\end{aligned} \tag{2.171}$$

and

$$\begin{aligned}
T_{1I} &= -\frac{1}{4} \frac{\Delta}{(2\pi)^3} \int_0^\infty 4\pi t^2 dt \left[\frac{K^4}{2c_I} \frac{1}{t^4 + K^2 t^2} \right] \\
&= -\frac{1}{2} \left(\frac{e^2}{DKT} \right) K.
\end{aligned} \tag{2.172}$$

This is just the Debye-Hückel result. Later when we remove nearest neighbor vacancy and interstitial configurations we shall modify these last two equations by introducing a factor $(1 + KR_c)$ in the denominator of the right hand sides where R_c denotes the nearest distance of approach of two defects.

2. Contributions from S^R and S^e

In Chapter IV we shall discuss the order in the concentration appropriate to the terms in S^R . At this point we merely state that for our purposes it is sufficient to consider only $S^R(2)$ and $S^R(3)$.

$S^R(2)$ is given by

$$S^R(2) = \sum_{i=I}^V \sum_{j=I}^{V^1} S_{ij}, \tag{2.173}$$

where

$$S_{ij} = \sum_{\nu \geq 3} \frac{c_i c_j}{2B^*} \sum_{\{1,j\}} \frac{m_{ij}^{\nu}}{\nu!} + \sum_{\nu \geq 0} \frac{c_i c_j}{2B} \sum_{1,j} \frac{m_{ij}}{1!} (-1_j). \quad (2.174)$$

In the first sum in equation (2.174) we start at $\nu=3$ because $\nu=1$ corresponds to S^e and $\nu=2$ corresponds to the lowest order cycle diagram. We can perform the sum over ν to get

$$S_{ij} = \sum_{\{1,j\}} \frac{c_i c_j}{2B^*} [e^{m_{ij}(1-\delta_{ij})} - 1] - \sum_{\{1,j\}} \delta_{ij} \frac{c_i c_j}{2B^*} - \sum_{\{1,j\}} \frac{c_i c_j}{2B^*} (m_{ij} + \frac{m_{ij}^2}{2}). \quad (2.175)$$

An alternative way of writing the preceding equation is

$$S_{ij} = \sum_{\{1,j\}} \frac{c_i c_j}{2B} (e^{m_{ij}} - 1) - S^{(1)} - S^{(2)} - \frac{c_i c_j}{2}, \quad (2.176)$$

where it is understood that upon summation R_{ij} is never allowed to be zero. The quantities $S^{(1)}$ and $S^{(2)}$ are defined by

$$S^{(1)} = \sum_{\{1,j\}} \frac{c_i c_j}{2B^*} m_{ij}$$

$$S^{(2)} = \sum_{\{1,j\}} \frac{c_i c_j}{2B^*} \frac{m_{ij}^2}{2}. \quad (2.177)$$

Proceeding as for $S^R(2)$ we find for $S^R(3)$

$$S^R(3) = \sum_{i=I}^V \sum_{j=I}^{V1} \sum_{k=I}^{V11} S_{ijk}. \quad (2.178)$$

where

$$S_{ijk} = \sum_{i,j,k} \frac{c_i c_j c_k}{3! B^*} [(e^{m_{ij}-1})(e^{m_{jk}-1-m_{jk}})(e^{m_{ki}-1-m_{ki}})] \quad (2.179)$$

with the same convention for R_{ij} as in equation (2.176). Contributions beyond $S^R(3)$ are too complicated to be of practical use.

The physical significance of the diagrams occurring in S^R is most easily seen by considering $S^R(2)$. In $S^R(2)$ the interactions are given by the m_{ij} which are essentially screened Coulomb interactions. Thus the defects lying between defects i and j are taken account of in the interaction between i and j by screening.

S^e is already in usable form. We combine it with $S^{(1)}$ to get contributions to the activity coefficients defined by

$$\begin{aligned} T_{2v} &= - \frac{B^*}{B_v} \frac{\partial}{\partial c_v} [S^e - S^{(1)}] \\ T_{2I} &= - \frac{B^*}{B_I} \frac{\partial}{\partial c_I} [S^e - S^{(1)}]. \end{aligned} \quad (2.180)$$

The remaining contributions are defined by

$$\begin{aligned} T_{3v} &= \frac{B^*}{B_v} \frac{\partial S^{(2)}}{\partial c_v} \\ T_{3I} &= \frac{B^*}{B_I} \frac{\partial S^{(2)}}{\partial c_I} \end{aligned}$$

$$\begin{aligned}
T_{4V} &= - \frac{B^*}{B_V} \frac{\partial}{\partial c_V} \left[\sum_{i=1}^2 \sum_{j=1}^2 \frac{c_i c_j}{2B^*} \left\{ \sum_{\{i,j\}} (e^{m_{ij}-1}) - B^* \right\} \right] \\
T_{4I} &= - \frac{B^*}{B_I} \frac{\partial}{\partial c_I} \left[\sum_{i=1}^2 \sum_{j=1}^2 \frac{c_i c_j}{2B^*} \left\{ \sum_{\{i,j\}} (e^{m_{ij}-1}) - B^* \right\} \right] \\
T_{5V} &= - \frac{B^*}{B_V} \frac{\partial S^{(R)}(3)}{\partial c_V} \\
T_{5I} &= - \frac{B^*}{B_I} \frac{\partial S^{(R)}(3)}{\partial c_I} . \quad (2.181)
\end{aligned}$$

Our approximations for the activity coefficients are therefore

$$\begin{aligned}
\log \gamma_V &= T_{1V} + T_{2V} + T_{3V} + T_{4V} + T_{5V} \\
\log \gamma_I &= T_{1I} + T_{2I} + T_{3I} + T_{4I} + T_{5I} . \quad (2.182)
\end{aligned}$$

We are now ready to obtain final forms. The derivatives appropriate for T_{2V} are

$$\begin{aligned}
\frac{B}{B_V} \frac{\partial}{\partial c_V} (S(e)) &= - \frac{\lambda}{4\pi B_V} \sum_j \delta_{V1} c_j \sum_{\{vj\}} \frac{Z_1 Z_j}{R_{1j}} \\
&= - \frac{\lambda}{4\pi B_V} \left[2c_V B_V \sum_{\{v\}} \frac{1}{R_{V0V}} + 2c_I B_V \sum_{\{I\}} \left(\frac{2}{R_{V0I}} \right) \right] \\
&= \frac{\lambda c}{\pi} \left[\sum_{\{2\}} \frac{1}{R_{V02}} - \sum_{\{1\}} \frac{1}{R_{V01}} \right] \quad (2.183)
\end{aligned}$$

and

$$\frac{B^*}{B_V} \frac{\partial}{\partial c_V} [s^{(1)}] = 2c \left[\sum_{\{1\}} m_{V_O 1} + \sum_{\{2\}} m_{V_O 2} \right] - \frac{KL}{8c} \frac{1}{2B_V} \sum_i \sum_j c_i c_j \sum_{ij} R_{ij} m_{ij} \quad (2.184)$$

where we have used

$$\frac{\partial m_{ij}}{\partial c_V} = - \frac{KL}{8c} R_{ij} m_{ij} (c = c_I = \frac{1}{2} c_V) \quad (2.185)$$

In equation (2.185) we assume that A_{ij} and L do not vary much with concentration compared with K . Writing the second term on the left hand side explicitly equation (2.184) becomes

$$\begin{aligned} \frac{B}{B_V} \frac{\partial}{\partial c_V} s^{(1)} &= \frac{2c\lambda}{4\pi} [A_{11} \sum_{\{1\}} e^{-KLR_{11}/R_{11} + A_{12} \sum_{\{2\}} e^{-KLR_{12}/R_{12}}] \\ &\quad - \frac{KL}{8c} \frac{1}{2B_V} [c_V^2 B_V \sum_{\{1\}} R_{11} m_{11} + 2c_V c_I B_V \sum_{\{2\}} 2R_{12} m_{12} \\ &\quad + c_I^2 B_I \sum_{\{2\}} (R_{22} m_{22} + R_{23} m_{23})] \\ &= \frac{K^2 \Delta}{8\pi} [A_{11} \sum_{\{1\}} \frac{e^{-KLR_{11}}}{R_{11}} + A_{12} \sum_{\{2\}} \frac{e^{-KLR_{12}}}{R_{12}}] \\ &\quad - \frac{KL}{8} \left[\frac{K^2 \Delta}{16\pi} \right] \left\{ 2A_{11} \sum_{\{1\}} e^{-KLR_{11}} + 4A_{12} \sum_{\{2\}} e^{-KLR_{12}} \right. \\ &\quad \left. + \sum_{\{2\}} (A_{22} e^{-KLR_{22}} + A_{23} e^{-KLR_{23}}) \right\}. \quad (2.186) \end{aligned}$$

Using equations (2.180), (2.183), and (2.186) we find

$$\begin{aligned}
 T_{2v} = & -\frac{K^2\Delta}{4\pi} \left[\sum_{\{2\}} \frac{1}{R_{12}} - \sum_{\{1\}} \frac{1}{R_{11}} \right] \\
 & + \frac{K^2\Delta}{8\pi} \left[A_{12} \sum_{\{2\}} \frac{e^{-KLR_{12}}}{R_{12}} + A_{11} \sum_{\{1\}} \frac{e^{-KLR_{11}}}{R_{11}} \right] \\
 & - \frac{K\Delta^2}{128\pi} \left[2A_{11} \sum_{\{1\}} e^{-KLR_{11}} + A_{22} \sum_{\{1\}} e^{-KLR_{11}} \right. \\
 & \left. + \sum_{\{2\}} (4A_{12} e^{-KLR_{12}} + A_{23} e^{-KLR_{23}}) \right]. \quad (2.187)
 \end{aligned}$$

Similarly we find

$$\begin{aligned}
 T_{2I} = & -\frac{K^2\Delta}{8\pi} \left[2 \sum_{\{2\}} \frac{1}{R_{12}} - \sum_{\{2\}} \left(\frac{1}{R_{22}} + \frac{1}{R_{23}} \right) \right] \\
 & + \frac{K^2\Delta}{16\pi} \left[\sum_{\{1\}} A_{22} \frac{e^{-KLR_{11}}}{R_{11}} + \sum_{\{2\}} \left(\frac{2A_{12} e^{-KLR_{12}}}{R_{12}} + A_{23} \frac{e^{-KLR_{23}}}{R_{23}} \right) \right] \\
 & - \frac{K\Delta^2}{128\pi} \left[2A_{11} \sum_{\{1\}} e^{-KLR_{11}} + A_{22} \sum_{\{1\}} e^{-KLR_{11}} \right. \\
 & \left. + \sum_{\{2\}} (4A_{12} e^{-KLR_{12}} + A_{23} e^{-KLR_{23}}) \right]. \quad (2.188)
 \end{aligned}$$

The derivatives appropriate for T_{3v} are

$$\begin{aligned}
 T_{3v} &= \frac{B^*}{B_v} \frac{\partial S^{(2)}}{\partial c_v} = \frac{1}{2B_v} \sum_i \sum_j \frac{\partial}{\partial c_v} \left[c_i c_j \sum_{\{i,j\}} \frac{m_{ij}^2}{2} \right] \\
 &= + \frac{1}{4B_v} 2 \sum_j c_j \sum_{\{v_j\}} (m_{vj})^2
 \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{4B_V} \sum_i \sum_j c_i c_j \sum_{\{1,j\}} \left(\frac{\partial m_{1j}}{\partial c_V} \right) m_{1j} \\
& = + \frac{1}{2B_V} [c_V B_V \sum_{\{1\}} m_{11}^2 + c_I B_V \sum_{\{2\}} 2m_{12}^2] \\
& - \frac{1}{2B_V} \frac{KL}{8c} \left[\sum_i \sum_j c_i c_j \sum_{\{1,j\}} R_{1j} m_{1j}^2 \right]. \quad (2.189)
\end{aligned}$$

Hence, substitution for the m_{1j} yields

$$\begin{aligned}
T_{3V} &= \frac{K \Delta^2}{256 \pi^2 c} \left[A_{11}^2 \sum_{\{1\}} \frac{e^{-2KLR_{11}}}{R_{11}^2} + A_{12}^2 \sum_{\{2\}} \frac{e^{-KLR_{12}}}{R_{12}^2} \right. \\
& - \frac{KL}{8} \frac{K \Delta^2}{256 \pi^2 c} [(2A_{11}^2 + A_{22}^2) \sum_{\{1\}} \frac{e^{-2KLR_{11}}}{R_{11}^2} \\
& \left. + 4A_{12}^2 \sum_{\{2\}} \frac{e^{-2KLR_{12}}}{R_{12}^2} + A_{23}^2 \sum_{\{2\}} \frac{e^{-2KLR_{23}}}{R_{23}^2} \right] \quad (2.190)
\end{aligned}$$

In an analogous fashion it is found that

$$\begin{aligned}
T_{3I} &= \frac{K \Delta^2}{512 \pi^2 c} \left[2A_{12}^2 \sum_{\{2\}} \frac{e^{-2KLR_{12}}}{R_{12}^2} + A_{23}^2 \sum_{\{2\}} \frac{e^{-2KLR_{23}}}{R_{23}^2} \right. \\
& \left. + A_{22}^2 \sum_{\{1\}} \frac{e^{-2KLR_{11}}}{R_{11}^2} \right] \\
& - \frac{KL}{8} \frac{K \Delta^2}{256 \pi^2 c} [(2A_{11}^2 + A_{22}^2) \sum_{\{1\}} \frac{e^{-2KLR_{11}}}{R_{11}^2}
\end{aligned}$$

$$+ 4A_{12}^2 \sum_{\{2\}} \frac{e^{-KLR_{12}}}{R_{12}} + A_{23}^2 \sum_{\{2\}} \frac{e^{-KLR_{23}}}{R_{23}}] . \quad (2.191)$$

For T_{4V} we have

$$\begin{aligned} T_{4V} &= \frac{B^*}{B_V} \frac{\partial}{\partial c_V} \frac{1}{2} \sum_i \sum_j c_i c_j - \frac{B^*}{B_V} \frac{\partial}{\partial c_V} \sum_i \sum_j \frac{c_i c_j}{2B^*} \sum_{\{1j\}} (e^{m_{1j}-1}) \\ &= + 9c - 2c \left[\sum_{\{1\}} (e^{m_{11}-1}) + \sum_{\{2\}} (e^{m_{12}-1}) \right] \\ &\quad + \frac{KLc}{8} \left[2 \sum_{\{1\}} R_{11} m_{11} e^{m_{11}} + \sum_{\{2\}} \{ 4R_{12} m_{12} e^{m_{12}} + R_{22} m_{22} e^{m_{22}} \right. \\ &\quad \left. + R_{23} m_{23} e^{m_{23}} \} \right] . \quad (2.192) \end{aligned}$$

Similarly, for T_{4I} we have

$$\begin{aligned} T_{4I} &= \frac{9c}{2} - c \left[2 \sum_{\{2\}} (e^{m_{12}-1}) + \sum_{\{2\}} (e^{m_{22}+m_{23}-2}) \right] \\ &\quad + \frac{KLc}{8} \left[2 \sum_{\{1\}} R_{11} m_{11} e^{m_{11}} + \sum_{\{2\}} \{ 4R_{12} m_{12} e^{m_{12}} \right. \\ &\quad \left. + R_{22} m_{22} e^{m_{22}} + R_{23} m_{23} e^{m_{23}} \} \right] . \quad (2.193) \end{aligned}$$

From equations (2.178) and (2.179) we obtain

$$\begin{aligned} S^{(R)}(3) &= \frac{c_I^3}{3!} \sum_{\{I_1, I_2, I_3\}} \frac{1}{B^*} (e^{m_{I_1 I_2}-1-m_{I_1 I_2}}) (e^{m_{I_2 I_3}-1-m_{I_2 I_3}}) \\ &\quad \cdot (e^{m_{I_3 I_1}-1}) + \frac{c_V^3}{3!} \sum_{\{V_1, V_2, V_3\}} \frac{1}{B} (e^{m_{V_1 V_2}-1-m_{V_1 V_2}}) (e^{m_{V_2 V_3}-1} \\ &\quad \cdot e^{-m_{V_2 V_3}}) \end{aligned}$$

$$\begin{aligned}
& \cdot (e^{m_{v_3} v_1 - 1}) + \frac{c_I c_v^2}{2!} \sum_{\{v_1, v_2, I_3\}} \frac{1}{B} [(e^{m_{v_1} v_2 - 1 - m_{v_1} v_2}) \\
& \cdot (e^{m_{v_2} I_3 - 1 - m_{v_2} I_3}) (e^{m_{I_2} v_1 - 1}) + (e^{m_{v_2} I_3 - 1 - m_{v_2} I_3}) (e^{m_{I_3} v_1 - 1 - m_{I_3} v_1}) \\
& \cdot (e^{m_{v_1} v_2 - 1})] + \frac{c_v c_I^2}{2!} \sum_{\{I_1, I_2, v_3\}} \frac{1}{B} [(e^{m_{I_1} I_2 - 1 - m_{I_1} I_2}) \\
& \cdot (e^{m_{I_2} v_3 - 1 - m_{I_2} v_3}) (e^{m_{v_3} I_1 - 1}) + (e^{m_{I_2} v_3 - 1 - m_{I_2} v_3}) (e^{m_{v_3} I_1 - 1 - m_{v_3} I_1}) \\
& \cdot (e^{m_{I_1} I_2 - 1})] \quad (2.194)
\end{aligned}$$

In each sum we pick an origin which brings out a factor of B_v or B_I (since $\sum_{\{I, v\}} = B_v \sum_{\{I\}} = B_I \sum_{\{v\}}$) to give

$$\begin{aligned}
S^{(R)}(3) &= \frac{c_I^3 B_I}{3! B^*} \sum_{\{I_1, I_2\}} (e^{m_{I_1} I_2 - 1 - m_{I_1} I_2}) (e^{m_{I_2} I_0 - 1 - m_{I_2} I_0}) \\
&\quad \cdot (e^{m_{I_0} I_1 - 1}) \\
&+ \frac{c_v^3 B_v}{3! B^*} \sum_{\{v_1, v_2\}} (e^{m_{v_0} v_1 - 1}) (e^{m_{v_1} v_2 - 1 - m_{v_1} v_2}) (e^{m_{v_2} v_0 - 1 - m_{v_2} v_0}) \\
&+ \frac{c_v^2 c_I B_v}{2 B^*} \sum_{\{v_1, I_1\}} [(e^{m_{v_0} v_1 - 1 - m_{v_0} v_1}) (e^{m_{v_1} I_1 - 1 - m_{v_1} I_1}) (e^{m_{I_1} v_0 - 1})]
\end{aligned}$$

$$\begin{aligned}
& + (e^{m_{v_0 v_1} - 1})(e^{m_{v_1 I_1} - 1 - m_{v_1 I_1}})(e^{m_{I_1 v_0} - 1 - m_{I_1 v_0}})] \\
& + \frac{c_v c_I^2}{2B^*} B_v \Sigma_{\{I_1, I_2\}} [(e^{m_{I_1 I_2} - 1})(e^{m_{I_2 v_0} - 1 - m_{I_2 v_0}})(e^{m_{v_0 I_1} - 1 - m_{v_0 I_1}}) \\
& + (e^{m_{I_1 I_2} - 1 - m_{I_1 I_2}})(e^{m_{I_2 v_0} - 1 - m_{I_2 v_0}})(e^{m_{v_0 I_1} - 1})] \\
\end{aligned} \tag{2.195}$$

We are now ready to find T_{v5} and T_{I5} . The expressions we shall obtain are quite lengthy so that it is worthwhile to separate T_{v5} and T_{I5} into pieces. Also, when all three defects are of the same type we have negligible contributions because something like

$$(e^{m_{v_1 v_2} - 1 - m_{v_1 v_2}})(e^{m_{v_2 v_0} - 1 - m_{v_2 v_0}})(e^{m_{v_0 v_1} - 1}) \tag{2.196}$$

is much smaller than

$$(e^{m_{v_1 v_2} - 1 - m_{v_1 v_2}})(e^{m_{v_2 I} - 1 - m_{v_2 I}})(e^{m_{v_2 I} - 1}) \tag{2.197}$$

for configurations in which all three defects are near each other. This is true because for nearby neighbors $m_{ij} > 1$ and is positive for oppositely charged defects and negative for defects of the same charge. Thus the only contributions of interest will be the derivatives of the last two terms on the right hand side of equation (2.195). In Fig. 3 we sketch these contributions. A dashed line between vertices 1 and

j represents the function $(e^{m_{ij}-1-m_{1j}})$ and a solid line represents the function $(e^{m_{ij}-1})$. For T_{v5} these contributions yield

$$\begin{aligned}
 T_{v5112}=T_{v5113}= & -\frac{2}{3} c^2 \sum_{\{1,2\}} [(e^{m_{v_o1}-1-m_{v_o1}})(e^{m_{12}-1-m_{12}})(e^{m_{2v_o}-1}) \\
 & + (e^{m_{v_o1}-1})(e^{m_{12}-1-m_{12}})(e^{m_{2v_o}-1-m_{2v_o}}) \\
 & - \frac{KL}{8} \{ R_{v_o1} m_{v_o1} (e^{m_{v_o1}-1})(e^{m_{12}-1-m_{12}})(e^{m_{2v_o}-1}) \\
 & + R_{12} m_{12} (e^{m_{12}-1})(e^{m_{v_o1}-1-m_{v_o1}})(e^{m_{2v_o}-1}) \\
 & + R_{2v_o} m_{2v_o} e^{m_{2v_o}} (e^{m_{v_o1}-1-m_{v_o1}})(e^{m_{12}-1-m_{12}}) \\
 & + R_{v_o1} m_{v_o1} e^{m_{v_o1}} (e^{m_{12}-1-m_{12}})(e^{m_{2v_o}-1-m_{2v_o}}) \\
 & + R_{12} m_{12} (e^{m_{12}-1})(e^{m_{v_o1}-1})(e^{m_{2v_o}-1-m_{2v_o}}) \\
 & + (e^{m_{v_o1}-1})(e^{m_{12}-1-m_{12}})(e^{m_{2v_o}-1}) R_{2v_o} m_{2v_o} \}] \\
 & (2.198)
 \end{aligned}$$

$$\begin{aligned}
 T_{v5122}=T_{v5133}= & -\frac{c^2}{6} \sum_{\{3,3\}} [(e^{m_{33^1}-1-m_{33^1}})(e^{m_{3^1v_o}-1-m_{3^1v_o}}) \\
 & \cdot (e^{m_{3v_o}-1})]
 \end{aligned}$$

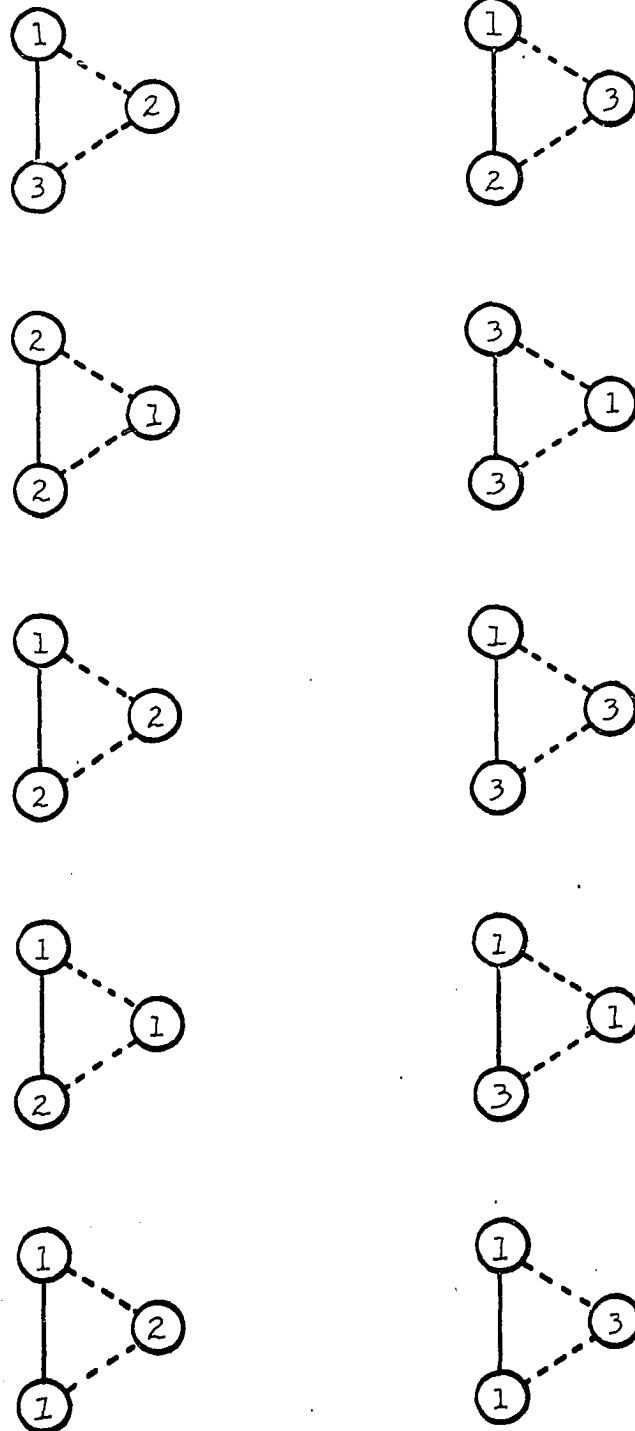


Fig. 3. Dominant contributions to $S^R(3)$

$$\begin{aligned}
& + (e^{m_{33}1} - 1)(e^{m_{v_o}3^1 - 1 - m_{v_o}3^1})(e^{m_{3v_o} - 1 - m_{3v_o}}) \\
& - \frac{KL}{8} \left\{ R_{33^1 m_{33^1}} (e^{m_{33^1}1} - 1)(e^{m_{3^1 v_o} - 1 - m_{3^1 v_o}})(e^{m_{v_o}3 - 1}) \right. \\
& + R_{3^1 v_o m_{3^1 v_o}} (e^{m_{3^1 v_o} - 1})(e^{m_{33^1}1 - 1 - m_{33^1}})(e^{m_{v_o}3 - 1}) \\
& + R_{v_o 3 m_{v_o} 3} e^{m_{v_o}3} (e^{m_{33^1}1 - 1 - m_{33^1}})(e^{m_{3^1 v_o} - 1 - m_{3^1 v_o}}) \\
& + R_{33^1 m_{33^1}} e^{m_{33^1}1} (e^{m_{3^1 v_o} - 1 - m_{3^1 v_o}})(e^{m_{v_o}3 - 1 - m_{v_o}3}) \\
& + R_{3^1 v_o m_{3^1 v_o}} (e^{m_{3^1 v_o} - 1})(e^{m_{33^1}1 - 1})(e^{m_{v_o}3 - 1 - m_{v_o}3}) \\
& \left. + R_{v_o 3 m_{v_o} 3} (e^{m_{v_o}3 - 1})(e^{m_{33^1}1 - 1})(e^{m_{3^1 v_o} - 1 - m_{3^1 v_o}}) \right\}
\end{aligned}$$

(2.199)

and T_{v5123} which has the same form as equation (2.199) with 3^1 replaced everywhere by 2. For T_{I5} the non negligible contributions are given by

$$\begin{aligned}
T_{I5112} = -c^2 \sum_{\{1,2\}} & [(e^{m_{1v_o} - 1 - m_{1v_o}})(e^{m_{12} - 1 - m_{12}})(e^{m_{2v_o} - 1}) \\
& + (e^{m_{v_o}1} - 1)(e^{m_{12} - 1 - m_{12}})(e^{m_{2v_o} - 1 - m_{2v_o}})]
\end{aligned}$$

$$\begin{aligned}
& - \frac{4}{KL} \left\{ R_{V_1 V_1}^{\circ} (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \right. \\
& + R_{12 m_{12}}^{\circ} (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \\
& + R_{2V m_{2V}}^{\circ} (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \\
& + R_{V_1 m_{V_1}}^{\circ} (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \\
& + R_{12 m_{12}}^{\circ} (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \\
& \left. + R_{2V m_{2V}}^{\circ} (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \right\} \cdot (2.200) \\
& T_{I5122} = T_{I5133} = \Sigma \left\{ R_{V_1 V_1}^{\circ} (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \right. \\
& + (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \\
& \left. - \frac{8}{KL} \left\{ R_{12 m_{12}}^{\circ} (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \right. \right. \\
& \left. + R_{2V m_{2V}}^{\circ} (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \right\} \\
& \left. + R_{V_1 V_1}^{\circ} (e_{m_{12} - 1 - m_{12}}) (e_{m_{2V} - 1}) \right\}
\end{aligned}$$

$$\begin{aligned}
& + R_{v_o 3} m_{v_o 3} e^{m_{v_o 3}} (e^{m_{33} 1} - 1 - m_{33} 1) (e^{m_{3' v_o} 1} - 1 - m_{3' v_o} 1) \\
& + R_{33' 1} m_{33' 1} e^{m_{33' 1}} (e^{m_{3' v_o} 1} - 1 - m_{3' v_o} 1) (e^{m_{v_o 3} 1} - 1 - m_{v_o 3} 1) \\
& + R_{3' v_o} m_{3' v_o} (e^{m_{3' v_o} 1} - 1) (e^{m_{v_o 3} 1} - 1 - m_{v_o 3} 1) (e^{m_{33' 1} 1} - 1) \\
& + R_{v_o 3} m_{v_o 3} (e^{m_{v_o 3} 1} - 1) (e^{m_{3' v_o} 1} - 1 - m_{3' v_o} 1) (e^{m_{33' 1} 1} - 1) \}], (2.201)
\end{aligned}$$

and T_{I5123} which has the same form as equation (2.201) with $3'$ replaced everywhere by 2. Equations (2.171), (2.172), (2.187), (2.188), (2.190), (2.191), (2.192), (2.193), (2.198), (2.199), and (2.201) along with the indicated forms for T_{v5123} and T_{I5123} can be substituted into equations (2.182) to give useful forms for the logarithms of the activity coefficients.

III. CALCULATION

The necessary input parameters for the self consistent computer calculation are the dielectric constant, the anion-cation separation, and the free energy of formation of a Frenkel defect pair. These parameters are available in the literature.

The anion-cation separation of silver chloride as a function of temperature was obtained from a polynomial fit to the data appearing in the thesis of Fouchaux (1963). The values for the temperature range under investigation are entered in Table 1.

Since in the formalism a Frenkel defect pair is added to the crystal keeping the configuration of the other defects fixed, the appropriate dielectric constant is that measured at frequencies high compared to the jump frequency of a defect. The silver interstitial is much more mobile than the vacancy. Considering only the interstitial to make jumps, the jump frequency is of form

$$w \sim fe^{-\phi/kT}, \quad (3.1)$$

where ϕ is the activation energy for the jump and f is the effective frequency of vibration of the interstitial. Let us make a rough estimate of w using the relation (Seitz 1940, p.549)

$$\mu = \frac{A^2 ew}{kT} \quad (3.2)$$

Table 1. Input dielectric constant and lattice parameter for temperature range 400°K to 750°K

$T(^{\circ}\text{K})$	D	$A(\times 10^8/\text{cm.})$
400	13.2	2.7844
410	13.4	2.7854
420	13.5	2.7864
430	13.6	2.7874
440	13.8	2.7884
450	13.9	2.7894
460	14.1	2.7904
470	14.3	2.7914
480	14.4	2.7924
490	14.6	2.7935
500	14.8	2.7946
510	15.0	2.7957
520	15.2	2.7968
530	15.4	2.7980
540	15.6	2.7991
550	15.8	2.8003
560	16.0	2.8015
570	16.3	2.8028
580	16.5	2.8040
590	16.8	2.8053
600	17.1	2.8066
610	17.4	2.8080

Table 1. (Continued)

$T(^{\circ}\text{K})$	D	$A(\times 10^8/\text{cm.})$
620	17.7	2.8094
630	18.1	2.8108
640	18.6	2.8123
650	19.0	2.8138
660	19.5	2.8154
670	20.1	2.8171
680	20.8	2.8189
690	21.5	2.8207
700	22.3	2.8227
710	23.2	2.8248
720	24.2	2.8270
730	25.3	2.8295
740	26.5	2.8321
750	27.9	2.8348

where μ is the mobility. Abbink (1964) gives for $T=571.4^{\circ}\text{K}$

$$\mu = 48.7 \frac{\text{cm}^2}{\text{volt sec.}} \times 10^{-4} \quad (3.3)$$

so that for the same temperature

$$w \approx 3 \times 10^{11}/\text{sec.} \quad (3.4)$$

We used the dielectric constant given by Smith (1962), which was measured at a frequency of $2.4 \times 10^{10}/\text{sec.}$, realizing that it would be a lower limit for the true value. The values obtained from this measurement are also entered in Table 1. It should be noted that the data taken by Smith went up to about 680°K . The values for temperatures higher than that were obtained by extrapolation.

We also used the low temperature value in our calculation for the whole temperature range to investigate the effects of the temperature dependence of the dielectric constant. The low temperature value used was $D=13.2$.

There is a variety of values available in the literature for the Frenkel pair formation energy. The value we chose was that determined by Abbink (1964). It is

$$F_{\text{FPA}} = 1.48\text{e.v.} - 10.4 \text{ k T.} \quad (3.5)$$

We also made the calculation using the Frenkel pair formation energy given by Müller (1965) which is

$$F_{\text{FPM}} = 1.25\text{e.v.} - 10.4 \text{ k T,} \quad (3.6)$$

where we have added on the temperature dependent part given by Abbink, an admittedly questionable procedure.

All the terms in equation (2.182) but T_{lv} and T_{li} involve lattice sums. T_{5v} and T_{5i} , the triangle diagram contributions, converge very rapidly and it was adequate to sum over only those triangle diagrams in which adjacent vertices were within $5A$ of each other. The other terms were summed explicitly out to ten anion-cation spacings. Beyond that distance the sums were replaced by integrals whose lower limits of integration were chosen by the method given in Appendix 3 of Born and Huang (1954).

In the terms involving lattice sums we left out the nearest neighbor configuration of an interstitial and vacancy. Since T_{lv} and T_{li} are just the Debye-Hückel result we removed nearest neighbors in the fashion of Lidiard (1957). This consists of introducing a factor $(1 + KR_c)$ where R_c is the smallest separation allowed between two defects.

We would now like to justify the removal of the nearest neighbor vacancy-interstitial configurations from the theory. The strong Coulomb interaction results in immediate annihilation of the defects when they are in this configuration. For an interaction between defects so close to one another, it is no longer appropriate to use a dielectric constant so that the interaction approaches e^2/R_{ij} rather than the smaller e^2/DR_{ij} . We cannot, therefore, consider this configuration to be an equilibrium configuration. In Fig. 4 we draw a qualitative picture

of the situation. $V(X)$ is the potential energy of the interstitial silver ion X away from a vacancy. X_1 , X_2 , and X_3 are the first, second, and third nearest neighbor interstitial positions respectively. If the silver ion receives enough thermal energy to reach X_1 it immediately relaxes back into the vacancy. But if the ion is thermally excited to X_2 or beyond it needs activation energy ϕ to move from its new position. A more exact analysis of $V(X)$ should show a decrease in its slope at X_1 because at that position the interstitial silver ion is near equilibrium with respect to the four nearest anions, but this effect should not be large enough to create a minimum at X_1 . We propose that removing these nearest neighbor configurations is a better approximation than assuming them to be equilibrium situations with the defects interacting via a dielectric constant.

For purposes of comparison we also made calculations using the same input parameters in the Debye-Hückel theory modified by the $(1 + KR_c)$ in the denominator of Δg . The R_c was chosen large enough to exclude nearest neighbor vacancy-interstitial configurations. This is somewhat analogous to the modification made by Lidiard for the case of divalent impurities (Lidiard 1954) in sodium chloride. He considered the nearest neighbor configuration of a divalent cation impurity and anion vacancy as a dipole with binding energy appreciably greater than kT . All such

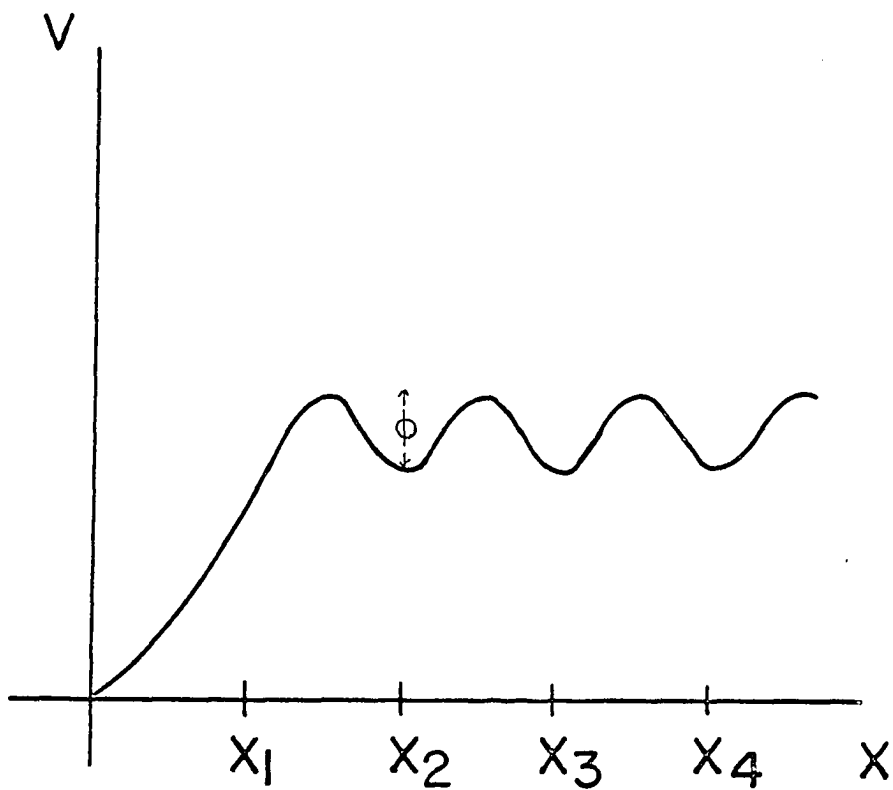
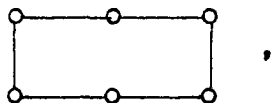


Fig. 4. Potential energy of silver interstitial versus distance from cation vacancy

dipoles were treated as non interacting and were removed from the theory by introducing the $(1 + KR_0)$ in the denominator of Δg . This is similar to what we have done except that the configurations we remove from the Debye-Hückel theory are treated as perfect crystal not dipoles.

IV. RESULTS AND DISCUSSION

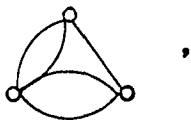
The physical significance of the diagrams contributing to $\log \gamma_v$ and $\log \gamma_I$ is of fundamental interest. The diagrams occurring in S^C are the easiest to understand. A typical diagram occurring in S^C is



where the bonds represent Coulomb interactions. We see that each defect is interacting with a defect on either side. Because of the $1/R_{ij}$ dependence of the Coulomb interaction the diagrams making the largest contribution are those in which the vertices correspond to the defects closest to one another. Thus at low concentrations the cycle diagrams make a good approximation for the activity coefficients because in that limit it is adequate to treat a defect as interacting with only the nearest neighboring defect. These cycle diagrams are similar to the ring diagrams of solution theory (Morita 1959). Salpeter (1958) demonstrates that if the Coulomb potential at the mean defect separation is small compared to kT then the ring summation problem results in the Debye-Hückel result. In this limit the types of diagrams contributing to his result have vertices which are connected to only the two neighboring vertices. This is the fundamental qualitative feature of our cycle diagrams. We previously indicated that the cycle diagrams

yield the Debye-Hückel result for our case.

At higher concentrations terms in S^R become important. The triangle diagrams of $S^R(3)$, for example, become important. A typical triangle diagram is



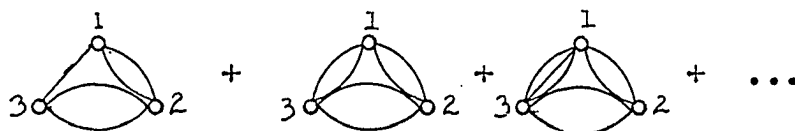
where each solid line represents an m_{ij} bond. Recall that m_{ij} is of form

$$m_{ij} \sim \frac{e^2}{DR_{ij}} e^{-KLR_{ij}} \quad (4.1)$$

and occurred as a result of summing over a defect chain, the ends of which were the defects i and j . This form for the interaction between defects i and j takes account of the presence of the intermediate defects via the screening factor $e^{-KLR_{ij}}$. This is in direct contrast to an individual cycle diagram where no intermediate defects were considered. However, upon summation over all the cycle diagrams we do get Debye-Hückel screening.

The appearance of multiple bonds is essentially a consequence of the original expansion of the exponential factor e^{BF} appearing in the configuration-dependent part of the partition function. For example, double bonds correspond to $F^2/2$. We in fact resummed these functions to get T_{5V} and T_{5I} . For example, consider the sum of

triangle diagrams

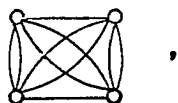


This corresponds to the series

$$\frac{m_{12}^2}{2!} \frac{m_{23}^2}{2!} (m_{31} + \frac{m_{31}^2}{2!} + \frac{m_{31}^3}{3!} + \dots) = \frac{m_{12}^2}{2!} \frac{m_{23}^2}{2!} (e^{m_{31}} - 1), \quad (4.2)$$

so that we can see in a rather indirect fashion that multiple bonds correspond to the higher order terms in the expansion of e^{BF} .

If we look at diagrams in S^R with more than three vertices, such as



we see that unlike the cycle diagrams vertices are allowed to interact with more vertices than just the nearest one. Thus the nature of the diagrams lead us to expect that these will contribute significantly at the higher concentrations. Further, it is evident that those diagrams whose vertices correspond to defects physically close together make the major contribution to S^R .

We would also like to point out to what order in the concentrations the various contributions to $\log \gamma_v$ and $\log \gamma_I$ correspond. S^C contributes the terms T_{lv} and T_{II} , the Debye-Hückel result. T_{lv} and T_{II} are of order \sqrt{c} .

S^R contributes T_{3v} , T_{3I} , T_{4v} , T_{4I} , T_{5v} , and T_{5I} (note that T_{2v} and T_{2I} are always small compared to the other terms). It is more appropriate to speak of the contributions from $S^R(2)$, $S^R(3)$, $S^R(4)$, etc. The contribution from $S^R(2)$ is of form

$$A_1 c + A_2 c^{3/2}, \quad (4.3)$$

that from $S^R(3)$ is of form

$$B_1 c^2 + B_2 c^{5/2}, \quad (4.4)$$

and that from $S^R(4)$ is of form

$$C_1 c^3 + C_2 c^{7/2}. \quad (4.5)$$

Further terms continue this pattern. The temperature dependent functions A_1 , A_2 , B_1 , B_2 , C_1 , and C_2 are to a good approximation concentration independent. These functions are, however, quite large and can be expected to contribute at high concentrations. For example, B_1 is of form

$$\sum_{i,j} \sum_{\{i,j\}} (e^{m_{ij} - 1 - m_{ij}}) (e^{m_{j0} - 1 - m_{j0}}) (e^{m_{0i} - 1}) \quad (4.6)$$

where the subscript 0 denotes the origin. The concentration dependence in B_1 occurs via the factor $A_{ij} e^{-KLR_{ij}}$ in m_{ij} . Since only diagrams with vertices corresponding to defects in close physical proximity contribute significantly $e^{-KLR_{ij}} \approx 1$ for these cases. The A_{ij} increase very slowly with increasing concentration; for example,

with $c_v = 1.2 \times 10^{-7}$ we have $A_{11} = -1.000$ and with $c_v = 3.6 \times 10^{-3}$ we have $A_{11} = -1.057$.

When we compare A_1 , B_1 , and C_1 we discover

$$C_1 > B_1 > A_1 \quad (4.7)$$

and similarly

$$C_2 > B_2 > A_2. \quad (4.8)$$

Consequently for sufficiently large defect concentrations the theory will diverge. However, at the same time the functions A_1 , A_2 etc. decrease with temperature so that the theory may not diverge over the entire temperature range. We shall see an example of this later.

Although numerical results can be obtained for A_1 , A_2 , B_1 , and B_2 it is impractical to attempt evaluation of further terms. For example, C_1 is of form

$$\sum_{j,k,l} \sum_{\{j,k,l\}} g_1(R_{oj})g_2(R_{jk})g_3(R_{kl})g_4(R_{lo})g_5(R_{jl})g_6(R_{ok}), \quad (4.9)$$

where the subscript o denotes the origin and the functions g are functions such as

$$g(R_{ij}) = (e^{m_{ij} - 1 - m_{ij}}). \quad (4.10)$$

In Table II we list the interstitial defect concentrations calculated from F_{FPA} (see equation (3.4)). C_{AO} denotes the value when the defects do not interact. C_{A1} is calculated employing the Allnatt-Cohen formalism without triangle diagram contributions and using the temperature dependent dielectric constant in the Coulomb potential.

The same calculation with a temperature independent dielectric constant ($D = 13.2$, the 400°K value) gives C_{A3} . To see the effect of the temperature dependent dielectric constant we have plotted Δg_1 and Δg_3 the changes in the free energy due to defect-defect interactions in C_{A1} and C_{A3} respectively. From equations (1.12) and (1.13)

$$\Delta g_1 = - \log \left(\frac{C_{A1}}{C_{A0}} \right) 2 k T \quad (4.11)$$

and

$$\Delta g_3 = - \log \left(\frac{C_{A3}}{C_{A0}} \right) 2 k T. \quad (4.12)$$

Δg_1 appears in Fig. 5 and Δg_3 appears in Fig. 6. Qualitatively, the two curves are similar except that Δg_1 reaches a maximum at $T \approx 690^\circ\text{K}$ while Δg_3 does not reach a maximum below the melting point. The same effect can be seen in the Lidiard calculation. The Lidiard calculation employing F_{FPA} and the temperature dependent dielectric constant yields the concentrations C_{A2} . The same calculation with a temperature independent dielectric constant ($D=13.2$) gives the concentrations C_{A4} . C_{A2} and C_{A4} also appear in Table 2. Δg_2 and Δg_4 appearing in Fig. 5 and Fig. 6, respectively, are given by

$$\Delta g_2 = - 2 k T \log \left(\frac{C_{A2}}{C_{A0}} \right) \quad (4.13)$$

Table 2. Interstitial defect concentrations calculated
from F_{FPA}

T	C_{A0}	C_{A1}	C_{A2}	C_{A3}	C_{A4}
400	6.05×10^{-8}	6.24×10^{-8}	6.23×10^{-8}	6.24×10^{-8}	6.23×10^{-8}
410	1.02×10^{-7}	1.06×10^{-7}	1.06×10^{-7}	1.06×10^{-7}	1.06×10^{-7}
420	1.68	1.76	1.75	1.76	1.76
430	2.70	2.85	2.84	2.86	2.85
440	4.26	4.54	4.51	4.56	4.53
450	6.57	7.08	7.03	7.13	7.07
460	9.95	1.08×10^{-6}	1.08×10^{-6}	1.10×10^{-6}	1.08×10^{-6}
470	1.48×10^{-6}	1.63	1.62	1.66	1.64
480	2.17	2.43	2.40	2.48	2.43
490	3.12	3.55	3.51	3.66	3.57
500	4.43	5.13	5.06	5.33	5.18
510	6.21	7.31	7.20	7.68	7.43
520	8.58	1.03×10^{-5}	1.01×10^{-5}	1.09×10^{-5}	1.05×10^{-5}
530	1.17×10^{-5}	1.43	1.41	1.55	1.48
540	1.58	1.98	1.94	2.16	2.06
550	2.11	2.70	2.64	3.00	2.85
560	2.79	3.64	3.57	4.12	3.90
570	3.66	4.86	4.77	5.62	5.32
580	4.74	6.44	6.34	7.59	7.19
590	6.09	8.43	8.32	1.02×10^{-4}	9.68
600	7.77	1.09×10^{-4}	1.08×10^{-4}	1.35	1.30×10^{-4}

Table 2. (Continued)

T	C _{A0}	C _{A1}	C _{A2}	C _{A3}	C _{A4}
610	9.82×10^{-5}	1.41×10^{-4}	1.40×10^{-5}	1.78×10^{-4}	1.72×10^{-4}
620	1.23×10^{-4}	1.80	1.80	2.33	2.28
630	1.54	2.27	2.28	3.01	3.01
640	1.90	2.83	2.87	3.86	3.94
650	2.34	3.51	3.58	4.92	5.14
660	2.85	4.31	4.44	6.20	6.65
670	3.47	5.24	5.43	7.75	8.57
680	4.19	6.31	6.59	9.60	1.09×10^{-3}
690	5.03	7.54	7.94	1.18×10^{-3}	1.39
700	6.00	8.94	9.47	1.43	1.75
710	7.14	1.05×10^{-3}	1.12×10^{-3}	1.72	2.18
720	8.44	1.23	1.32	2.05	2.70
730	9.94	1.42	1.53	2.42	3.30
740	1.17×10^{-3}	1.63	1.78	2.82	4.01
750	1.36	1.87	2.04	3.26	4.83

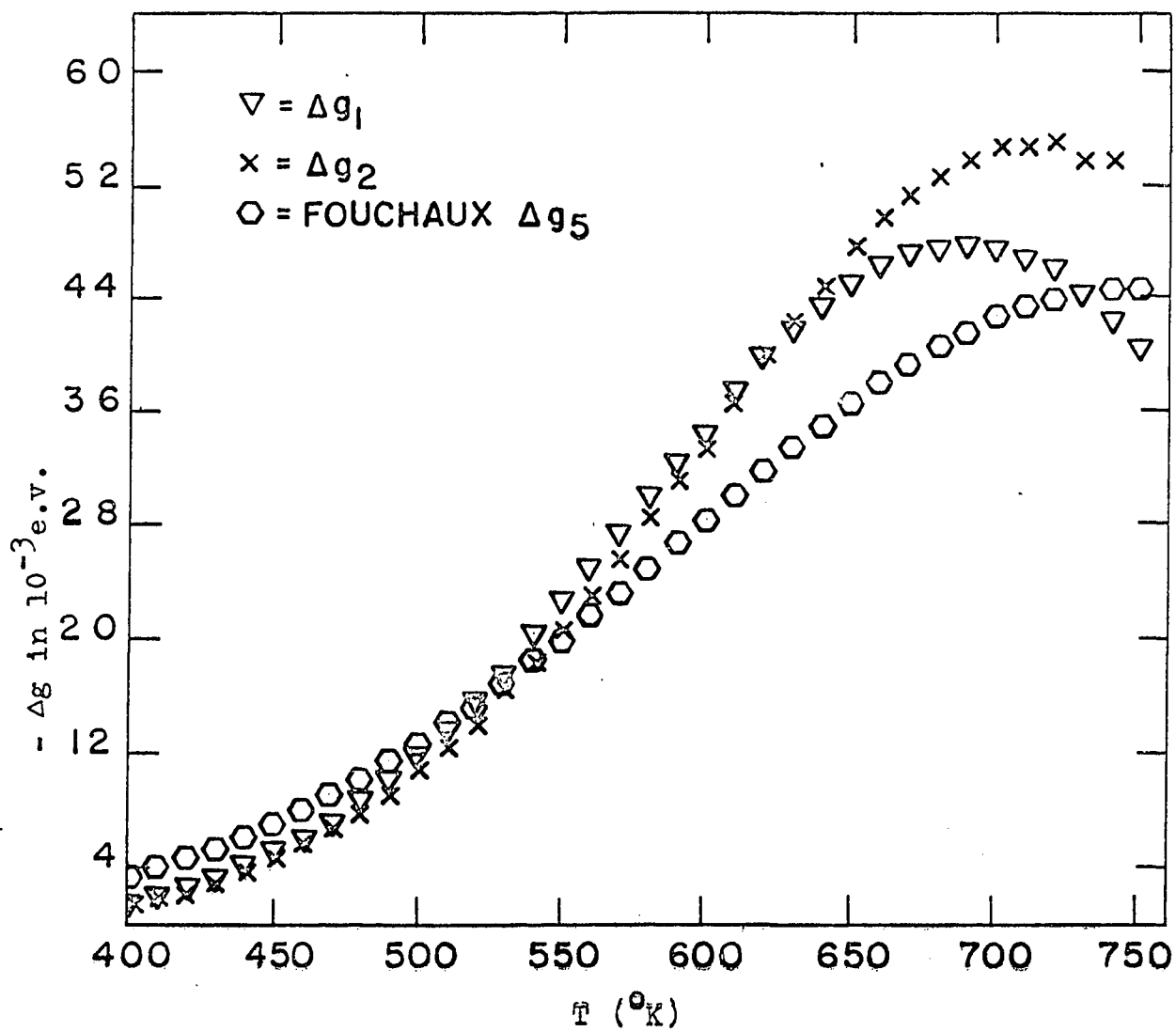


Fig. 5. Δg calculated from F_{FFA} and the temperature dependent dielectric constant

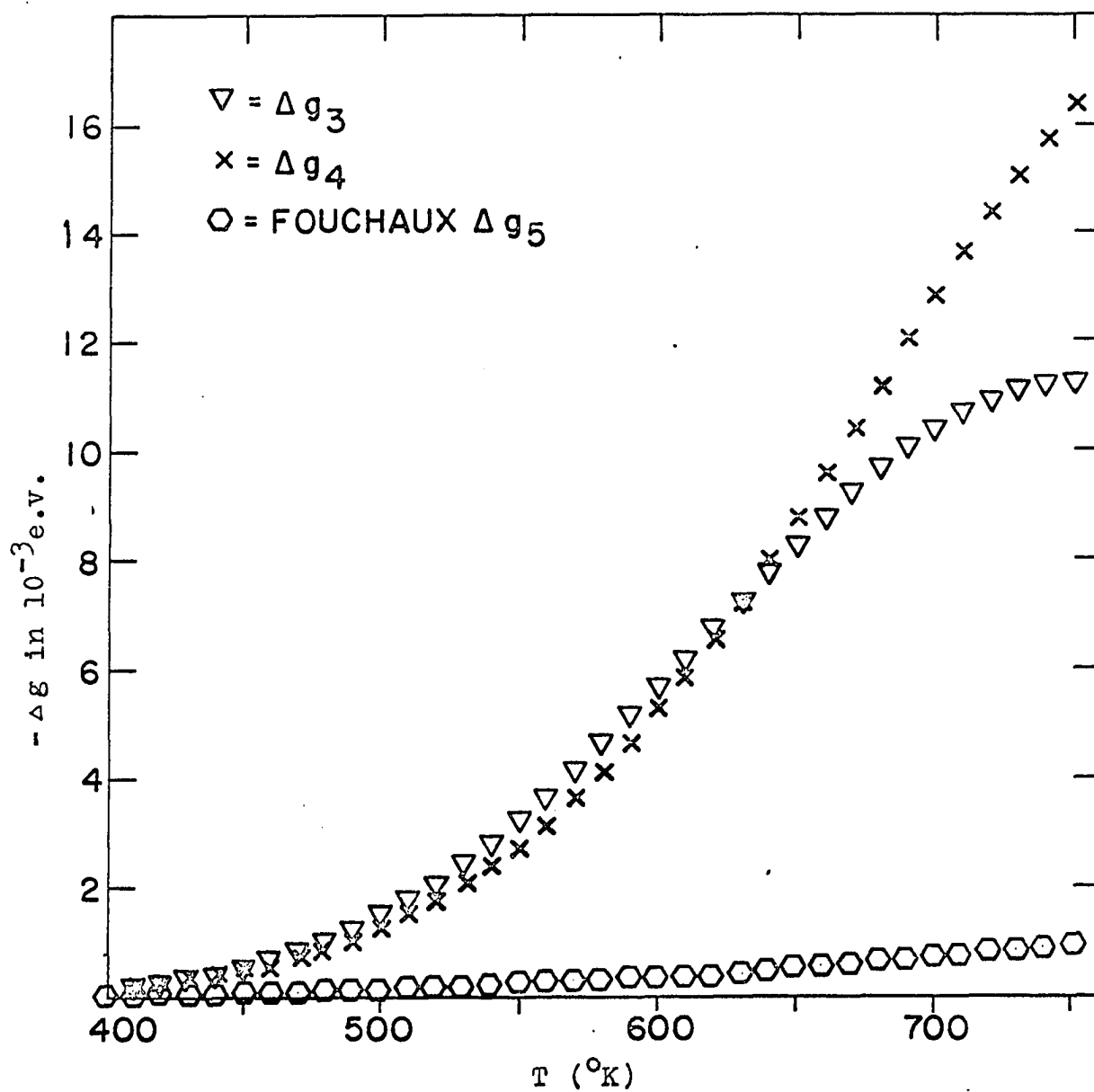


Fig. 6. Δg calculated from F_{FPA} and the temperature independent dielectric constant

and

$$\Delta g_4 = - 2 k T \log\left(\frac{C_{Al}}{C_{AO}}\right). \quad (4.14)$$

Comparison of Δg_2 and Δg_4 again demonstrates that the most striking effect of the temperature dependence of the dielectric constant is the appearance of a maximum in Δg below melting. In the Appendix we show that for the simple case of the Debye-Hückel potential Δg has a maximum above the melting temperature for a temperature independent dielectric constant. If $(1 + KR_c)$ and a temperature dependent dielectric constant are included in the denominator of Δg this maximum is moved to temperatures lower than melting.

Our final evidence that the occurrence of the maximum in Δg at lower temperature is an effect of the temperature dependence of the dielectric constant is found in the thesis of Fouchaux (1963). Using dimensional arguments alone he derives an expression for Δg ,

$$\Delta g_5 = - 3.5 e^2 c^{1/3}/AD. \quad (4.15)$$

We plot Δg_5 in Fig. 5 and Fig. 6 using a temperature dependent and temperature independent dielectric constant, respectively. Again a maximum appears for the case of the temperature dependent dielectric constant although not quite below melting. Δg_5 is much too flat. Its agreement with Δg_1 at melting would seem to be fortuitous.

To see the differences between the Allnatt-Cohen formalism and the Lidiard theory we compare C_{A1} and C_{A2} . This is done most clearly by comparing Δg_1 and Δg_2 as they appear in Fig. 5. Qualitatively the two curves are similar except that as higher temperatures are reached Δg_1 drops significantly below Δg_2 . Note that this feature is preserved for the same calculations but using a temperature independent dielectric constant (see Δg_3 and Δg_4 in Fig. 6). An alternative way of saying the same thing is that the maximum in Δg_1 occurs at a lower temperature than does the maximum in Δg_2 . This occurs because the Debye-Hückel approach breaks down at the high concentrations. This is evident in the calculation for C_{A1} . At 620°K Δg_1 becomes less than Δg_3 . At this temperature we found

$$T_{1v} = T_{1I} = .37338 \quad (4.16)$$

corresponding to the Lidiard result. The remaining terms gave

$$\begin{aligned} T_{2v} + T_{3v} + T_{4v} &= - .00065 \\ T_{2I} + T_{3I} + T_{4I} &= - .00053 \end{aligned} \quad (4.17)$$

so that the Lidiard and Allnatt-Cohen results are nearly equal. However, at 720°K Δg_1 is considerably lower than Δg_3 . At this temperature we found

$$T_{1v} = T_{1I} = .42831 \quad (4.18)$$

corresponding to the Lidiard result. The remaining terms gave

$$T_{2v} + T_{3v} + T_{4v} = - .06766$$

$$T_{2I} + T_{3I} + T_{4I} = - .06246 \quad (4.19)$$

so that the agreement between the Lidiard and Allnatt-Cohen results is not nearly as good as at 620°K.

In the calculation employing F_{FPA} the triangle diagram contributions are not important. This is demonstrated in Table 3 where C_A is the interstitial defect concentration including triangle diagrams and using the temperature dependent dielectric constant. It does not depart more than two percent from C_{A1} .

Also appearing in Table 3 is C_{A5} . C_{A5} and C_{A1} resulted from identical calculations except that C_{A5} used $R_c = A$ and C_{A1} used $R_c = \sqrt{3} A/2$. These choices of R_c are the next nearest and nearest neighbor positions, respectively. Recall that R_c is the closest separation allowed by two defects. For example, we do not wish two interstitial silver ions to get closer than A . The appropriate choice of R_c for our case does not allow the nearest neighbor configuration of a vacancy and interstitial to occur. There are really two ways of looking at R_c . If say defects are separated and interacting for $R \geq R_c$ we should use $R_c = A$. But if we say a defect pair is a neutral entity unless $R > R_c$ then we should use $R_c = \frac{\sqrt{3}A}{2}$. The latter is our choice (Fowler and Guggenheim 1949, p.552). Since C_{A5} has a larger R_c it

leads to a smaller Δg and consequently $C_{A5} < C_{A1}$. This is evident in Table 3. A choice of R_c anywhere in the range $\sqrt{3}A/2$ to A does not exclude any more lattice sites and consequently we would hope that a slight variation in R_c should not cause a large variation in the results of the calculation. C_{A1} and C_{A2} do not differ by more than three percent at any temperature.

At melting (728°K) C_{A1} is 1.38×10^{-3} . Since this is an interstitial concentration we double it to get a Frenkel pair concentration of 2.8×10^{-3} . The conductivity measurements of Ebert and Teltow (1955) give 3.5×10^{-3} at melting, twenty-five percent higher than our calculated value. We see that use of equation (3.4) for the free energy of formation of a Frenkel defect pair in the Allnatt-Cohen formalism gives concentrations which are in fair agreement with experiment. The calculation converges rapidly in this case with $S^R(3)$ giving only a very small contribution. At the same time it must be realized that the result given by Ebert and Teltow was obtained by a curve fitting procedure which of a necessity involves a dependence on the model used.

Let us now discuss the case where the free energy of formation of Frenkel defects is given by equation (3.5). As we mentioned earlier it is not legitimate to use the entropy of formation given by Abbink (1964) with the enthalpy of formation given by Müller (1965). Equation (3.5) would seem to be a lower limit for the free energy of formation because

Table 3. Interstitial defect concentrations calculated from F_{FPA} including triangle diagrams

T	C_{Al}	C_A	C_{A5}
400	6.24×10^{-8}	6.26×10^{-8}	6.20×10^{-8}
410	1.06×10^{-7}	1.06×10^{-7}	1.05×10^{-7}
420	1.76	1.76	1.75
430	2.85	2.87	2.84
440	4.54	4.56	4.51
450	7.08	7.13	7.04
460	1.08×10^{-6}	1.09×10^{-6}	1.08×10^{-6}
470	1.63	1.65	1.62
480	2.43	2.46	2.41
490	3.55	3.60	3.53
500	5.13	5.21	5.10
510	7.31	7.43	7.27
520	1.03×10^{-5}	1.05×10^{-5}	1.02×10^{-5}
530	1.43	1.46	1.43
540	1.98	2.01	1.96
550	2.70	2.75	2.68
560	3.64	3.71	3.61
570	4.86	4.93	4.82
580	6.44	6.53	6.38
590	8.43	8.53	8.35
600	1.09×10^{-4}	1.10×10^{-4}	1.08×10^{-4}
610	1.41	1.42	1.39

Table 3. (Continued)

T	C_{A1}	C_A	C_{A5}
620	1.80×10^{-4}	1.81×10^{-4}	1.78×10^{-4}
630	2.27	2.27	2.24
640	2.83	2.83	2.79
650	3.51	3.51	3.46
660	4.31	4.31	4.24
670	5.24	5.23	5.15
680	6.31	6.29	6.20
690	7.54	7.52	7.41
700	8.94	8.92	8.78
710	1.05×10^{-3}	1.05×10^{-3}	1.03×10^{-3}
720	1.22	1.22	1.20
730	1.42	1.42	1.39
740	1.63	1.63	1.61
750	1.87	1.87	1.84

if we use it to compute C_{VO} , the defect pair concentration for no defect-defect interactions, we get 1.3×10^{-2} at melting. This is almost four times higher than the value of found experimentally by Ebert and Teltow (1955) which includes defect-defect interactions. However, the use of equation (3.5) is of interest in examining the range of validity of the Allnatt-Cohen formalism.

If the Frenkel pair formation energy is given by equation (3.5) the Lidiard theory is not at all adequate except at very low temperatures. From 400°K to 550°K the contributions to the activity coefficients from $S^R(2)$ and $S^R(3)$ are of the same order of magnitude. This is the example we spoke of immediately following inequality (4.8).

In Table 4 we enter the resulting concentrations.

C_{M0} is the concentration when interactions among defects are ignored. C_{M1} and C_{M2} are calculated with the Allnatt-Cohen formalism employing equation (3.5) for the free energy of formation. C_{M1} does not include contributions from $S^R(3)$ while C_{M2} does. Note that at high T C_{M1} and C_{M2} are close to one another. The contribution from $S^R(3)$ at high T is about a tenth of that from $S^R(2)$. Thus the difficulty with the convergence of the theory lies in the intermediate temperature range 400°K to 550°K . To see why the formalism converges again at high T consider the expression (4.6) for the form of B_1 . Since $m_{ij} \sim \frac{1}{D}$ and D rises with T (see Table 1) B_1 decreases with T .

Table 4. Interstitial defect concentrations calculated from F_{FPM}

T	C_{MO}	C_{M1}	C_{M2}
400	1.97×10^{-6}	2.36×10^{-6}	6.77×10^{-6}
410	3.05	3.76	
420	4.63	5.89	1.62×10^{-5}
430	6.90	9.08	
440	1.01×10^{-5}	1.37×10^{-5}	3.35
450	1.45	2.04	
460	2.06	2.99	6.16
470	2.87	4.30	
480	3.95	6.13	1.04×10^{-4}
490	5.36	8.56	
500	7.19	1.18×10^{-4}	1.63
510	9.53	1.62	
520	1.25×10^{-4}	2.18	2.59
530	1.62	2.90	
540	2.09	3.82	4.12
550	2.66	4.99	
560	3.36	6.44	6.56
570	4.21	8.19	
580	5.23	1.04×10^{-3}	1.02×10^{-3}
590	6.46	1.30	
600	7.92	1.60	1.57
610	9.64	1.97	

Table 4. (Continued)

T	C _{M0}	C _{M1}	C _{M2}
620	1.17×10^{-3}	2.39×10^{-3}	2.34×10^{-3}
630	1.40	2.86	
640	1.68	3.39	3.33
650	1.99	4.00	
660	2.36	4.65	4.59
670	2.77	5.35	
680	3.25	6.09	6.03
690	3.78	6.88	
700	4.39	7.69	7.66
710	5.08	8.53	8.50
720	5.84	9.38	9.35
730	6.70	1.02×10^{-2}	1.02
740	7.66	1.11	1.11
750	8.72	1.20	1.20

A_1 similarly decreases but $A_1 c$ does not decrease as rapidly as $B_1 c^2$. Similar remarks apply to A_2 and B_2 . If we had used the temperature independent dielectric constant ($D = 13.2$) the divergence would have appeared everywhere above 400°K .

We note here that the results C_{M1} and C_{M2} were not calculated self consistently. A self consistent calculation would have been successful in the high T (above 550°K) region, however, since the entropy term in equation (3.5) is questionable we merely examined the qualitative results rather than the numerical results. We did examine the self consistent method for the low T region. After a few iterations the low T (400°K to 550°K) concentrations diverged. This lack of convergence suggested to us that not all choices of input parameters are consistent with the equations of the theory. To investigate this we considered the special case of the Debye-Hückel potential, V_{DH} , which we write

$$\frac{V_{DH}}{2kT} = - \sqrt{\pi c_v} \left(\frac{e^2}{ADkT} \right)^{3/2}, \quad (4.20)$$

where

$$c_v = c_{v0} e^{-V_{DH}/2kT}. \quad (4.21)$$

Letting

$$y = - V_{DH}/2kT \quad (4.22)$$

we combine equations (4.20) and (4.21) to get

$$y = P(T)e^{y/2}, \quad (4.23)$$

where

$$P(T) = \sqrt{\pi} c_{v0} \left(\frac{e^2}{ADkT} \right)^{3/2}. \quad (4.24)$$

Equation (4.23) can be solved graphically (see Fig. 7).

Whether or not equation (4.23) has a solution depends on the value of $P(T)$. For

$$P(T) < 0.7 \quad (4.25)$$

we observe from Fig. 7 that there are two roots to equation (4.23). The root which is physically meaningful is the one closer to the origin because V_{DH} decreases with decreasing defect concentration for this root. This is also the root to which a self consistent calculation will converge by starting the calculation with $c_v = c_{v0}$. As $P(T)$ approaches and becomes larger than 0.7 these two roots approach each other and after they meet there are no roots to equation (4.14). For the Frenkel pair formation energy given by equation (3.4) and the temperature dependent dielectric constant we obtain

$$P(T) = 0.32 \text{ at } 700^\circ\text{K}$$

which is within the region of two roots. However, for the Frenkel pair formation energy given by equation (3.5) and the temperature dependent dielectric constant we have

$$P(T) = 0.87 \text{ at } 700^\circ\text{K}$$

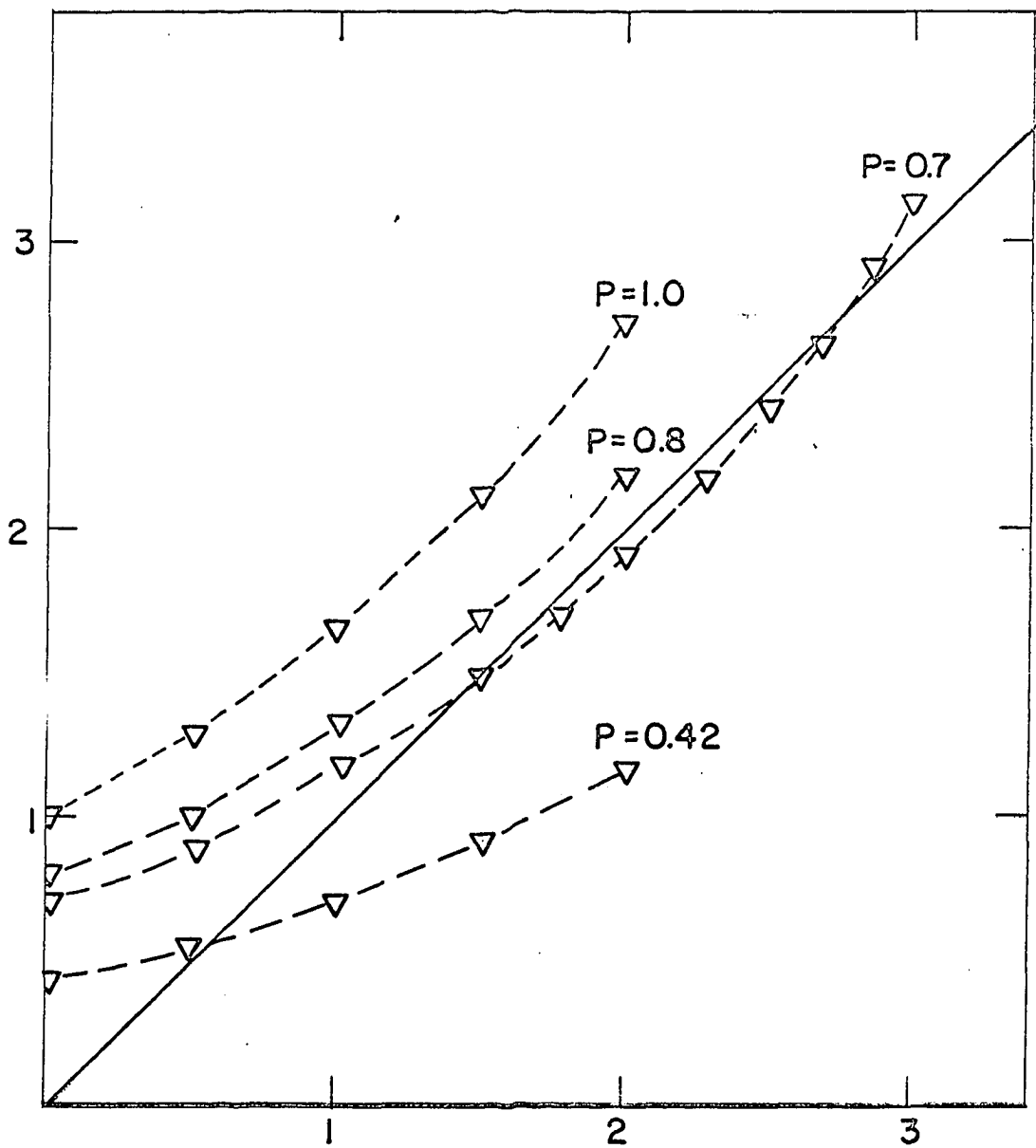


Fig. 7. Graphical solution of $y = Pe^{y/2}$.
Dashed lines are $f(y) = Pe^{y/2}$. Solid line is $f(y) = y$.

which is in the region of no roots. We infer from this simple example that there are possible choices of input parameters that will not be consistent with the Allnatt-Cohen formalism. We cannot conclude that such choices of input parameters (e.g. F_{FPM} from equation (3.5)) are incorrect, however. It may well be that a more realistic and exact treatment of configurations in which defects are close to each other would resolve the inconsistency.

V. SUMMARY

The Allnatt-Cohen formalism was quite adequate for a Frenkel pair formation free energy given by 1.48 e.v. - 10.4 kT. The resulting defect concentration at melting was 2.8×10^{-3} , about twenty-five percent less than the experimental value (Ebert and Teltow 1955). The agreement between Lidiard theory and this formalism was good below $\sim 620^\circ\text{K}$. Above 620°K the Lidiard theory remained a first approximation and at melting gave a concentration about seven percent above the Allnatt-Cohen result.

Use of a smaller free energy of formation, 1.25 e.v. - 10.4 kT, indicated that in this case the Lidiard theory was adequate only below 400°K . From 400°K to 550°K the result of the Lidiard theory was the first term in a slowly converging series resulting from the Allnatt-Cohen formalism using a temperature dependent dielectric constant. At high T the rising dielectric constant weakened the Coulomb interaction sufficiently so that the theory converged.

There were two striking results of our investigation. The first was the occurrence of a maximum in Δg , the change in the free energy of formation due to defect-defect interactions. We showed that this maximum was to be expected even in the case of the Lidiard theory. The second interesting result was that not all input parameters are consistent with the equations of the theory. We investigated this fact for

the simple case of the Debye-Hückel potential to find that there are a region of no roots to the equation for Δg , a region of two roots, and a point where there is one root separating the no root and two root regions.

VI. APPENDIX

To see that Δg has a relative maximum we consider the specific case of the Debye-Hückel potential,

$$\Delta g = V_{DH} = - \sqrt{\pi} c_v \left(\frac{e^2}{ADkT} \right)^{3/2} 2kT. \quad (5.1)$$

In a first approximation we have that

$$c_v = c_{v0} \quad (5.2)$$

and

$$D = 13.2 \neq D(T). \quad (5.3)$$

To find the relative maximum under these crude assumptions we have

$$\frac{d(\Delta g)}{dT} = 0. \quad (5.4)$$

We also have

$$c_{v0} = \sqrt{2} e^{-F_{FP}/2kT} = \sqrt{2} e^{-(h_{FP} - TS_{FP})/2kT}. \quad (5.5)$$

where h_{FP} is the enthalpy of formation and S_{FP} is the entropy change on addition of a Frenkel pair. From equations (5.1) through (5.5) we get

$$\frac{d}{dT} \left(\frac{e^{-h_{FP}/4kT}}{\sqrt{T}} \right) = 0 \quad (5.6)$$

Taking the derivative yields

$$T_m = h_{FP}/2k \quad (5.7)$$

as the temperature at which Δg reaches a maximum. For the value of h_{FP} given by Abbink this gives

$$T_m = \frac{1.48e.v.}{2k} \approx 1700^\circ K. \quad (5.8)$$

In the cases of the Allnatt-Cohen and Lidiard theories, there is a $(1 + KR_c)$ in the denominator of Δg as well, which moves the maximum to lower temperature. To see this consider $(1 + KR_c)^{-1}$ as an amplitude factor multiplying V_{DH} . Since $(1 + KR_c)^{-1}$ decreases with increasing temperature it will move the maximum in Δg to lower temperature. If in addition we use the temperature dependent dielectric constant we obtain the same effect because D also appears in the denominator of Δg and D^{-1} decreases with increasing temperature (see Table 1).

VII. REFERENCES

- Abbink, H. C. 1964. Conductivity of silver chloride crystals containing copper (I) or cadmium ions. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology.
- Abbink, H. C. and Martin J. 1966. J. Phys. Chem. Solids 27: 205.
- Allnatt, A. and Cohen, M. H. 1964a. J. Chem. Phys. 40: 1860.
- Allnatt, A. and Cohen, M. H. 1964b. J. Chem. Phys. 40: 1871.
- Allnatt, A. and Jacobs, P. 1962. Trans. Faraday Soc. 58: 116.
- Born, M. and Bradburn, M. 1943. Proc. Cambridge Phil. Soc. 39: 104.
- Born, M. and Huang, K. 1954. Dynamical theory of crystal lattices. Oxford, England, Oxford at the Clarendon Press.
- Christy, R. W. and Lawson, A. W. 1951. J. Chem. Phys. 19: 517.
- Compton, W. D. and Maurer, R. 1956. J. Phys. Chem. Solids 1: 191.
- Debye, P. and Hückel, E. 1923. Physikal. Zeit. 24:185.
- Ebert, I. and Teltow, J. 1955. Ann. Physik 15: 268.
- Ewald, P. 1921. Ann. Physik 64: 253.
- Fouchaux, R. 1963. Measurements of thermal expansion and thermal equilibrium defects in pure silver chloride. Unpublished Ph.D. thesis. Urbana, Illinois, Library, University of Illinois.
- Fouchaux, R. and Simmons, R. O. 1964. Phys. Rev. 136: A1664.
- Fowler, R. and Guggenheim, E. 1949. Statistical thermodynamics. Cambridge, England, Cambridge at the University Press.
- Frenkel, J. 1926. Z. Physik 35: 652.
- Hanlon, J. E. 1960. J. Chem. Phys. 32: 1492.

- Kliwer, K. L. 1966. J. Phys. Chem. Solids 27: 705.
- Koch, E. and Wagner, C. 1937. Z. Physik. Chem. B38: 295.
- Kurnick, S. 1952. J. Chem. Phys. 20: 218.
- Kurosawa, T. 1957. J. Phys. Soc. Japan 12: 338.
- Lidiard, A. B. 1954. Phys. Rev. 94: 29.
- Lidiard, A. B. 1957. Handbuch der Physik 20: 246.
- London, F. 1930. Z. Physik 63: 245.
- Mayer, J. 1933a. J. Chem. Phys. 1: 270.
- Mayer, J. 1933b. J. Chem. Phys. 1: 327.
- Mayer, J. 1950. J. Chem. Phys. 18: 1426.
- McMillan, W. and Mayer, J. 1945. J. Chem. Phys. 13: 276.
- Misra, R. D. 1940. Proc. Cambridge, Phil. Soc. 36: 173.
- Morita, T. 1959. Prog. Theoret. Phys. 21: 361.
- Mott, N. F. and Gurney, R. W. 1964. Electronic processes in ionic crystals. New York, N.Y., Dover Publications, Inc.
- Müller, P. 1965. Phys. Stat. Sol. 12: 775.
- Neville, E. H. 1953. Disc. Faraday Soc. 16: 72.
- Salpeter, E. E. 1958. Annals of Physics 5: 183.
- Seitz, F. 1940. The modern theory of solids. New York, N.Y., McGraw Hill Book Company, Inc.
- Smith, G. C. 1962. Cornell University Materials Science Center, Report 51.
- Teltow, J. 1949. Ann. Physik 5: 63.
- van Santen, J. H. 1950. Philips Research Repts. 5: 282.
- Wagner, C. and Schottky, W. 1931. Z. Physik. Chem. B11: 163.

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